PIGMENTS

INORGANIC

Inorganic pigments are an integral part of numerous decorative, protective, and functional coating systems, eg, automotive finishes, marine paints, industrial coatings, traffic paints, maintenance paints, and exterior and interior oil, alkyd or latex house paints (see Coatings; Paint). In addition, they provide mass coloration for fibers, plastics, paper, rubber, elastomers, glass, cement, glazes, and porcelain enamels. They are colorants in printing inks, cosmetics, and markers, eg, crayons (see Colorants). Some are used for pigmentation of magnetic tape (qv) and others as fillers (qv) for paper products. A few pigments that were used prior to the discovery of Prussian blue in 1704 were cinnabar [19122-79-3], malachite [1319-53-5], Egyptian blue [10279-60-4], lapis lazuli [1302-85-8], white lead [1344-36-1], and carbon [7440-44-0] (1–5).

Inorganic pigments belong to numerous chemical classes including elements, oxides, sulfides, chromates, silicates, phosphates, and carbonates. Available pigments are whites, eg, titanium dioxide, zinc oxide, and zinc sulfide; reds, eg, cadmium sulfide selenide [12214-12-9], and iron oxide [1345-25-1]; yellows, eg, cadmium sulfide, lead chromate [7758-97-6], and iron oxide; greens, eg, chromium oxide green; blues, eg, iron, ultramarine, and cobalt blues; and blacks, eg, carbon black. There also are metallic flakes and many natural and synthetic extender pigments, eg, kaolinite, mica, calcium carbonate, silica, barium sulfate, and talc.

Pigments can be colored, colorless, black, white, or metallic. Generally they are solids of small particle size and remain insoluble or relatively so in the medium or binder in which they are dispersed. Color production results from the pigment's selective absorption of visible light; large pigment particles also may scatter light and thereby influence the opacity of the binder. Pigments provide protective functions: by absorbing uv and other radiation, they prevent degradation and embrittlement of film or substrate; by changing film permeability, they increase durability; or, by chemical interactions with substrates, they can retard corrosion (see Corrosion and corrosion inhibitors). They can act as fungistats and antistatic agents (qv) or can be used to control rheological properties (see Fungicides; Rheological measurements).

Properties and characteristics that are factors in pigment selection include hue, tint, or undertone hue; tinctorial strength; brightness; texture; dispersibility; opacity; transparency; oil absorption; lightfastness; weatherability; solvent, chemical, heat, moisture, bleed, and migration resistance; flow, leveling, and other rheological properties; and binder reactivity. Properties of pigments are not only a function of the chemical composition but are related to other physical and chemical characteristics such as particle size, particle shape, particle size distribution, and the nature of the pigment's surface. In addition, surface contaminants, eg, water and/or water solubles, can influence the behavior of pigmented systems. Unless otherwise noted, most property values given in the tables and in the text are listed in ref. 6.

Various inorganic pigments and their Colour Index names and numbers, CAS Registry Numbers, chemical compositions, and specifications are listed alphabetically in Table 1. More specifications and trade designations are given in ref. 7. Descriptions of chemical and physical tests as applied to pigments are published by ASTM as well as in refs. 7 and 8.

Properties

Color. Clean, bright, intense, reproducible hues are most important for all pigments. The basic hue of a pigment is fixed by its chemical constitution, but modifications of brightness, cleanliness, and intensity are affected by refractive index differences between the pigment and the medium in which it is dispersed. Other influencing factors include particle size, shape, and size distribution, and crystal habit.

The two most commonly used systems to describe color quantitatively are the Munsell and CIE systems. With the CIE system, a spectral reflectance curve is determined for the dispersed pigment. The general shape of the curve does not vary if the pigment is dispersed with different binders. Normally, the pigment manufacturer evaluates the self color as a masstone in a given binder and the color as a tint when reduced with white. From juxtaposition comparisons, evaluations against a standard provide information on hue shifts, depth of shade, brightness, cleanness, bronzing, oil absorption, flatness, texture, and strength (see Color).

When inorganic and organic compounds are exposed to a wide energy range of electromagnetic radiation, electronic transitions within the compounds occur, ie, electrons are activated from ground state energy levels to higher, excited, permissible energy levels by selective absorption of known frequencies of the radiation, and those frequencies that are not absorbed are reflected. Selective absorption of energies of 1.72–3.1 eV, ie, the energies of visible light, produce color.

Color development in many inorganic pigments involves transition metals and bonding between metal ions with surrounding, geometrically arranged molecules and anions or ligands. The arrangement of the ligands about a central metallic ion causes electronic (crystal field) transitions. The color of pigments, eg, the iron oxides and chromium oxide green, results from such crystal field transitions (see Coordination compounds).

A different structural model characterizes color development in pigments containing nontransition elements. For example, in lead chromate, the intense yellow color results from a charge-transfer process, by which an electron from the oxygen atom is involved in a transition to the chromium atom within CrO_4^{2-}. The lead atom also must contribute to color production because lead chromate is yellow, whereas silver chromate is red.

The color of iron blue, $Fe(III)NH_4[Fe(II)(CN)_6]$, results from the presence of iron in two different oxidation states in the molecule and the resultant charge transfer between them. The color of cadmium sulfide is based on its semiconductor properties and the charge-transfer transitions between the valence band and the conductance band (see Semiconductors). The color of ultramarine blue results from electronic transitions within S_3^-, which is contained in the zeolite structure of this complex sodium

Table 1. Listing of Inorganic Pigments, Colour Index Name and Number, CAS Registry Number, and Specifications

Colorant	CI name and number	CAS Registry Number	Chemical composition	Specifications
alumina hydrate	Pigment White 24, CI 77002	[1332-73-6]	$AlHO_5$	TT-P-320C
aluminum flake	Pigment Metal 1, CI 77000	[7429-90-5]	Al	ASTM D 962-66
				TT-P-325a
				MIL-P-15144A
antimony oxide	Pigment White 11, CI 77052	[1309-64-4]	Sb_2O_3	MIL-E-17970C
asbestos				
barium metaborate[a]		[12001-29-5]	$3MgO.2SiO_2.2H_2O$	
		[13701-59-2]	$BaB_2O_4.H_2O$	
barytes	Pigment White 22, CI 77120	[7727-43-7]	$BaSO_4$	ASTM D 602-42
barium sulfate, natural				
bismuth oxychloride		[7787-59-9]	$BiOCl$	
black iron oxide				
natural	Pigment Black 11	[1317-61-9]	Fe_3O_4	TT-P-390
synthetic	Pigment Black 11, CI 77499	[12227-89-3]	Fe_3O_4	ASTM D 769-48
blanc fixe	Pigment White 21, CI 77120	[7727-43-7]	$BaSO_4$	ASTM D 602-42
barium sulfate, synthetic				
bone black	Pigment Black 9, CI 77267	[8021-99-6]	C	
bronze powders	Pigment Metal 2, CI 77400	[7440-50-8]	Cu/Zn	ASTM D 267-41
cadmium sulfide	Pigment Yellow 37, CI 77199	[1306-23-6]	CdS	TT-P-342
cadmium sulfide	Pigment Yellow 35, CI 77117	[8048-07-5]	$CdS/ZnS/BaSO_4, CdS/BaSO_4$	TT-P-342
lithopone				
cadmium orange	Pigment Orange 20, CI 77196	[12656-57-4]	$CdS/CdSe, CdS/CdSe/BaSO_4$	TT-P-341a
pure and lithopone				
cadmium red	Pigment Red 108, CI 77202	[58339-34-7]	$CdSe/CdS, CdSe/CdS/BaSO_4$	TT-P-341a
pure and lithopone				
calcium carbonate	Pigment White 18, CI 77220	[471-34-1]	$CaCO_3$	ASTM D 1199-69
natural and synthetic				Maritime 52-MA-524b
calcium molybdate		[7789-82-4]	$CaMoO_4$	MIL-C-15198A
calcium plumbate		[12013-69-3]	$2CaO.PbO_2$	
calcium silicate		[1344-95-2]		British Standard 3699
carbon black	Pigment Black 7, CI 77266	[1333-86-4]	C	
chrome green	Pigment Green 15, CI 77510/	[1308-38-9]	mixture of iron blue and	TT-P-345
	77603	[1344-37-2]	chrome yellow	ASTM D 212-47; D 213-47

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Common name	Pigment / CI	CAS	Composition	Standards
chrome green	Pigment Green 15, CI 77510/77603	[1308-38-9] [1344-37-2]	mixture of iron blue and chrome yellow	TT-P-345 ASTM D 212-47; D 213-47
chrome orange	Pigment Orange 21, CI 77601	[1344-38-3]	$PbCrO_4 \cdot PbO$	British Standard 303:1963 TT-P-346b ASTM D 211-67T
chrome yellow medium	Pigment Yellow 34, CI 77600	[1344-37-2] [7758-97-6]	$PbCrO_4$	TT-P-346b ASTM D 211-67T
primrose, light, lemon	Pigment Yellow 34, CI 77603	[1344-37-2]	$PbCrO_4 \cdot PbSO_4$	TT-P-346b ASTM D 211-67T
chromium oxide green	Pigment Green 17, CI 77288	[1308-38-9]	Cr_2O_3	TT-P-347 ASTM D 263-46
dihydrate	Pigment Green 18, CI 77289	[12001-99-9]	$Cr_2O_3 \cdot 2H_2O$	
cobalt blue	Pigment Blue 28, CI 77346	[1345-16-0]	$CoO \cdot Al_2O_3$	
copper chromite black		[12018-10-9]	$Cu(CrO_2)_2$	
cuprous oxide		[1317-39-1]	Cu_2O	
ferrite yellow	Pigment Yellow 42, CI 77492	[51274-00-1] [11100-07-5]	iron oxide hydrate	MIL-P-15169B MIL-P-15166B ASTM D 912-65 TT-P-548a ASTM D 768-47
gloss white	Pigment White 23, CI 77122	[8049-83-0]	$3BaSO_4 \cdot Al(OH)_3$	
graphite	Pigment Black 10, CI 77265	[7782-42-5]	C	U.S. Government SS-G-659a MIL-G-6711 MIL-G-155a
iron blue	Pigment Blue 27, CI 77510	[14038-43-8]	$FeNH_4\,Fe(CN)_6$	TT-P-385 ASTM D 261-47
iron oxide, micaceous		[1309-37-1]	Fe_2O_3	
kaolin, aluminum silicate	Pigment White 19, CI 77005	[1318-74-7]	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	
lamp black	Pigment Black 6, CI 77266	[1333-86-4]	C	ASTM D 603-66
lead carbonate, basic	Pigment White 1, CI 77597	[1344-36-1]	$2PbCO_3 \cdot Pb(OH)_2$	
lead phosphite, dibasic		[24824-71-3]	$2PbO\ PbHPO_3 \cdot \tfrac{1}{2}H_2O$	TT-W-251g ASTM D 81-43 British Standard 239
lead silicate, basic	Pigment White 16, CI 77625	[10099-76-0]		
lead sulfate, basic	Pigment White 2, CI 77633	[7446-14-2] [1344-42-9]	$PbSO_4 - PbSO_4 \cdot PbO$	TT-W-261C ASTM D 82-44
lithopone	Pigment White 5, CI 77115	[1345-05-7]	$BaSO_4 \cdot ZnS$	TT-L-426 TT-P-400 ASTM D 477-45 British Standard 239, 296
manganese violet	Pigment Violet 16, CI 77742	[10101-66-3]	$NH_4MnP_2O_7$	

Table 1 (*continued*)

Colorant	CI name and number	CAS Registry Number	Chemical composition	Specifications
Mercadium orange, mercury–cadmium orange	Pigment Orange 23, CI 77201	[1345-09-1]	CdS/HgS	ASTM D 911-65 MIL-M-15177A
Mercadium red, mercury–cadmium red	Pigment Red 113, CI 77201	[1345-09-1]	CdS/HgS	TT-P-405 ASTM D 84-51 ASTM D 607 MIL-M-15176 MIL-P-15176 TT-P-410 ASTM D 2218-67
mercuric oxide red yellow		[21908-53-2]	HgO	
metallic brown, brown iron oxide	Pigment Brown 6, CI 77499	[12227-89-3]		
mica, aluminum potassium silicate	Pigment White 20, CI 77019	[12001-26-2]	$3Al_2O_3.K_2O.6SiO_2.2H_2O$	
molybdate orange	Pigment Red 104, CI 77605	[12656-85-8] [12709-98-7] [37244-96-5]	$25PbCrO_4.4PbMoO_4.PbSO_4$	
nepheline syenite				
nickel titanate	Pigment Yellow 53, CI 77788	[8007-18-9]	$NiO.Sb_2O_3.20TiO_2$	
novaculite	Pigment White 27, CI 77811	[7631-86-9]	SiO_2	
pumice		[1332-09-8]		
red iron oxide, natural and synthetic	Pigment Red 101, CI 77491	[8011-97-0]	Fe_2O_3, variable composition	TT-P-405 ASTM D 84-51 TT-R-191d ASTM D 83-41
red lead	Pigment Red 105, CI 77578	[1314-41-6]	Pb_3O_4	
satin white		[12344-48-8]		
siennas, natural	Pigment Brown 7, CI 77499	[12227-89-3]	iron oxides (varying percentages FeO) [1345-27-3]	TT-P-438 ASTM D 765-48
silica, aerogel and hydrogel		[7631-86-9]	SiO_2	
amorphous	Pigment White 27, CI 77811	[7631-86-9]	SiO_2	
crystalline	Pigment White 27, CI 77811	[7531-86-9]	SiO_2	ASTM D 604-42
diatomaceous	Pigment White 27, CI 77811	[7631-86-9]	SiO_2	
sodium alumino silicate				Maritime 52-MA-522a MIL-D-20550B British Standard 1795
strontium chromate	Pigment Yellow 32, CI 77839	[1344-00-9] [12677-00-8]	$SrCrO_4$	MIL-P-23377 ASTM D 1649-65

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Name	Colour Index	CAS Number	Formula	Standards
strontium molybdate		[13470-04-7]	$SrMoO_4$	
talc, magnesium silicate	Pigment White 26, CI 77718	[14807-96-6]	$3MgO.4SiO_2.H_2O$	TT-P-403a ASTM D 605-69 Maritime 52-MA-523b MIL-P-15173A British Standard 1795
titanium dioxide	Pigment White 6, CI 77891 anatase rutile	[62338-64-1] [13463-67-7] [1317-70-0] [1317-80-0]	TiO_2	TT-P-442 ASTM D 476 British Standard 851
ultramarine blue	Pigment Blue 29, CI 77007	[1317-97-1]	$Na_{(6-8)}Al_6Si_6O_{24}S_{(2-4)}$	TT-U-450 ASTM D 262-47 FDA 21CFR Part 121
ultramarine violet	Pigment Violet 15, CI 77007	[12769-96-9]	$H_2N_{(4-6)}Al_6Si_6O_{24}S_2$	
umbers, natural	Pigment Brown 7, CI 77499	[12227-89-3]	iron oxides (varying percent- ages FeO) [1345-27-3]	TT-P-455
vermilion	Pigment Red 106, CI 77766	[1344-48-5] [14567-51-2]	HgS	ASTM D 763-48
wollastonite				
zinc chromate, basic	Pigment Yellow 36, CI 77955	[50922-29-7]	$4Zn(OH)_2.ZnCrO_4$	MIL-C-8514C MIL-P-1532SC MIL-P-15930B
zinc dust	Pigment Metal 6, CI 77945	[7440-66-6]	Zn	TT-P-460 ASTM D 250
	Pigment Black 16, CI 77945	[7440-66-6]	Zn	TT-P-460 ASTM D 250
zinc ferrite	Pigment Brown 11, CI 77495	[12063-19-3]	$ZnO.Fe_2O_3$	
zinc molybdate		[13767-32-3]	$ZnMoO_4$	
zinc molybdate, basic		[61583-60-6]	$xZnO.ZnMoO_4$	
zinc oxide	Pigment White 4, CI 77947	[1314-13-2]	ZnO	TT-P-463a ASTM D 79-44 British Standard 254, 2876
zinc phosphate	Pigment White 32, CI 77964	[7779-90-0]	$Zn_3(PO_4)_2.2H_2O$	TT-P-400
zinc sulfide	Pigment White 7, CI 77975	[1314-98-3]	ZnS	ASTM D 477-45
zinc yellow	Pigment Yellow 36, CI 77955	[37300-23-5]	$4ZnO.K_2O.4CrO_3.3H_2O$	TT-P-465 ASTM D 478-49
zircon	Pigment White 12, CI 77990	[14940-68-2]	$ZrSiO_4$	
zirconium oxide		[1314-23-4]	ZrO_2	

a Modified.

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aluminosulfosilicate pigment (see Molecular sieves). Factors such as crystal structure and particle size modify the color produced. Color origin in inorganic compounds is discussed in refs. 9–10.

Crystal Habit and Crystal Modification.   Few inorganic pigments are amorphous, eg, they are characterized by cubic, rhombic, or hexagonal lattice structures. Crystal defects and modification of crystal lattice patterns influence pigment characteristics. Where multiple lattice structures exist for a given pigment, controls must be exercised during formation to obtain the proper crystal habit and, thereby, prevent incorrect hue and other unwanted pigment properties.

Inorganic pigments display polymorphism, eg, titanium dioxide occurs in three crystal forms, of which rutile [1317-80-2] and anatase [1317-70-0] are commercially important (see Figs. 1 and 2). Both are tetragonal with the titanium ion octahedrally
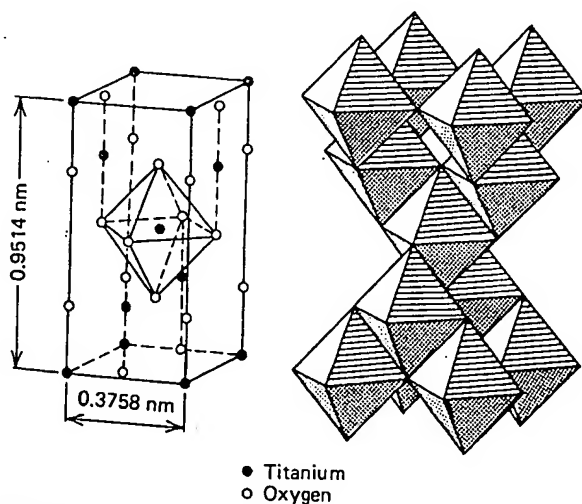
• Titanium
○ Oxygen

Figure 1.   Crystal structure of anatase titanium dioxide.
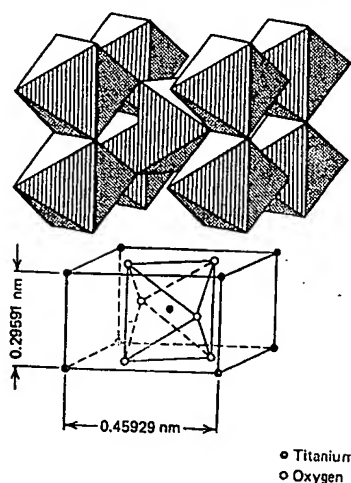
○ Titanium
○ Oxygen

Figure 2.   Crystal structure of rutile titanium dioxide.

bonded to six oxygen ions. However, the position of the octahedra in the lattice and the number of molecules of TiO_2 in the unit cell differ. Anatase contains four TiO_2 molecules per unit cell and rutile contains two. Polymorphism also occurs in lead chromates and is utilized to produce a wide range of hues. Lead chromate and lead sulfate are polymorphic; the stable form of lead chromate is monoclinic and that of lead sulfate is orthorhombic. Solid solutions of $PbCrO_4$ and $PbSO_4$ can be prepared at nearly similar chemical compositions but in different crystal structures.

X-ray diffraction data for a primrose and a light chrome yellow where the $PbCrO_4$ to $PbSO_4$ ratio is 3.29 and 3.23, respectively, possessed these four strongest reflections corresponding to interplanar spacings d(nm) and their intensities (I/I_1); for the primrose: 0.307(100); 0.340(83); 0.328(60); 0.437(54); for the light yellow; 0.326(100), 0.303(66); 0.346(56) and 0.435(42) (11).

Other polymorphic pigments are calcium carbonate that is synthetically precipitated in either the hexagonal calcite form or the orthorhombic aragonite form; vermilion which occurs in two main enantiomorphic forms, ie, red or α-HgS and black or α'-HgS; and some iron oxide browns that change color on heating because of crystal change from γ to α.

Particle Size. The average ultimate particle size of most commercial pigments, excluding extenders, is $0.01-1.0$-μm dia. Extenders and some pigments are as large as 100 μm with average diameters of as much as 50 μm. Particle sizes of commercially available inorganic pigments are shown in Table 2.

Hiding power of a pigment depends primarily upon the ability of the dispersed particles to scatter light; factors that influence hiding power are refractive index and particle size. The smaller the pigment particles, the more light is scattered; the effective maximum in particle size is that of titanium dioxide white, ie, $0.2-0.3$ μm. The effective particle size for most pigments should be ca one-half the wavelength of visible light. Tinting strength also is related to particle size and approaches a maximum at similar values for some inorganic pigments and at lower particle size values for carbon blacks. Size reduction causes the following observed shifts in hue: red becomes yellower, orange becomes yellower, yellow becomes greener, green becomes yellower, blue becomes greener, and violet becomes redder.

Most pigments are sold as powders and, as such, most of the particles are aggregated or agglomerated. As pigments are prepared, crystallites and single crystals form and convert to ultimate or primary particles. Eventually, the particles form aggregates and agglomerates or, if in suspensions, flocculates.

Primary particles are discrete units; they may be single crystals or crystallites,

Table 2.   Particle Size of Some Inorganic Pigments, μm[a]

Pigment	Particle size, μm
iron blue	0.01-0.2
titanium dioxide	0.2-0.3
red iron oxide	0.3-4.0
natural crystalline silica	1.5-9.0
strontium chromate	0.3-20.0
hydrated aluminum oxide	0.4-60.0
micaceous iron oxide	5.0-100.0

[a] Refs. 6-7.

ie, combinations of single crystals that appear as units under x ray and are characterized by a coherent space lattice. They assume a variety of shapes, eg, cube, sphere, needle, etc. Aggregates are primary particles that are randomly joined at their surfaces. The interior surfaces are unavailable to wetting, thus the total surface area of the aggregate is less than the sum of the surfaces of the individual particles. Agglomerates are primary particles that are joined at their corners and edges and their interior surfaces are readily available to wetting. Thus, the total surface area of the agglomerate is not significantly smaller than the sum of the surfaces of the individual particles. Flocculates occur in liquid systems when the dispersed pigment forms loose combinations or agglomerates as effected by van der Waals or electrostatic forces. Usually flocculates can be broken down by stirring.

Microscopy, gas absorption, and sedimentation techniques are used to determine particle size. The maximum working particle size of dry pigments is ca 44 μm; particles of this size pass through a 45-μm (325-mesh) screen with less than 1% retention. A more narrow particle size distribution results in more consistent and better working properties, eg, better gloss and cleaner hues (See Size measurement of particles).

Particle Shape. Pigment particles can be spheroidal, acicular or needlelike, or laminar or platy. In some applications, particle shape affects the final properties of the pigment more profoundly than does size. Shape influences flow and settling and, in some instances, paint film durability. Transmission-electron photomicrographs of some commercially available colored pigments are shown in Figures 3a, b, c, and d.

Surface Area. Surface areas must be wetted properly by a vehicle to achieve complete dispersion. Surface areas of carbon blacks are 6–1100 m^2/g pigment in contrast to those of most other pigments, ie, 1–100 m^2/g. There are a few inorganic pigments with surface areas of 100–400 m^2/g.

The BET method is widely used for determining surface area of a pigment powder. The method is based on the adsorption of nitrogen at extremely low temperatures and low pressures; some values are listed in Table 3 (12–13).

Manufacture

Many inorganic pigments are manufactured by precipitation and control is exercised over many factors that influence the properties of the product. Of primary concern are the purity of raw materials, the concentration and the sequence of combining the reactant solutions, the temperature of the precipitation, the acidity or alkalinity during precipitation, the addition rate of reactants, rate of slurry agitation, the presence of modifiers or particle-size control agents during precipitation, addition of stabilizers where necessary after precipitation, heat treatment of the aqueous pigment slurry, and the type of treatment applied to the pigment surface.

After precipitating, the pigment is filtered and then washed to remove undesirable soluble salts. Filtration can be accomplished with plate-and-frame filter presses or rotary filter equipment, and the completeness of washing can be determined by measuring the conductance of the effluent. Reduction of soluble-salt content aids in reducing particle aggregation during drying; tray, belt, drum, and spray dryers can be utilized. Final processing involves grinding, classifying, and packaging. Particle aggregation can be reduced and pigment properties can be developed further by flushing pigment presscake into a suitable vehicle; this technique is especially suitable
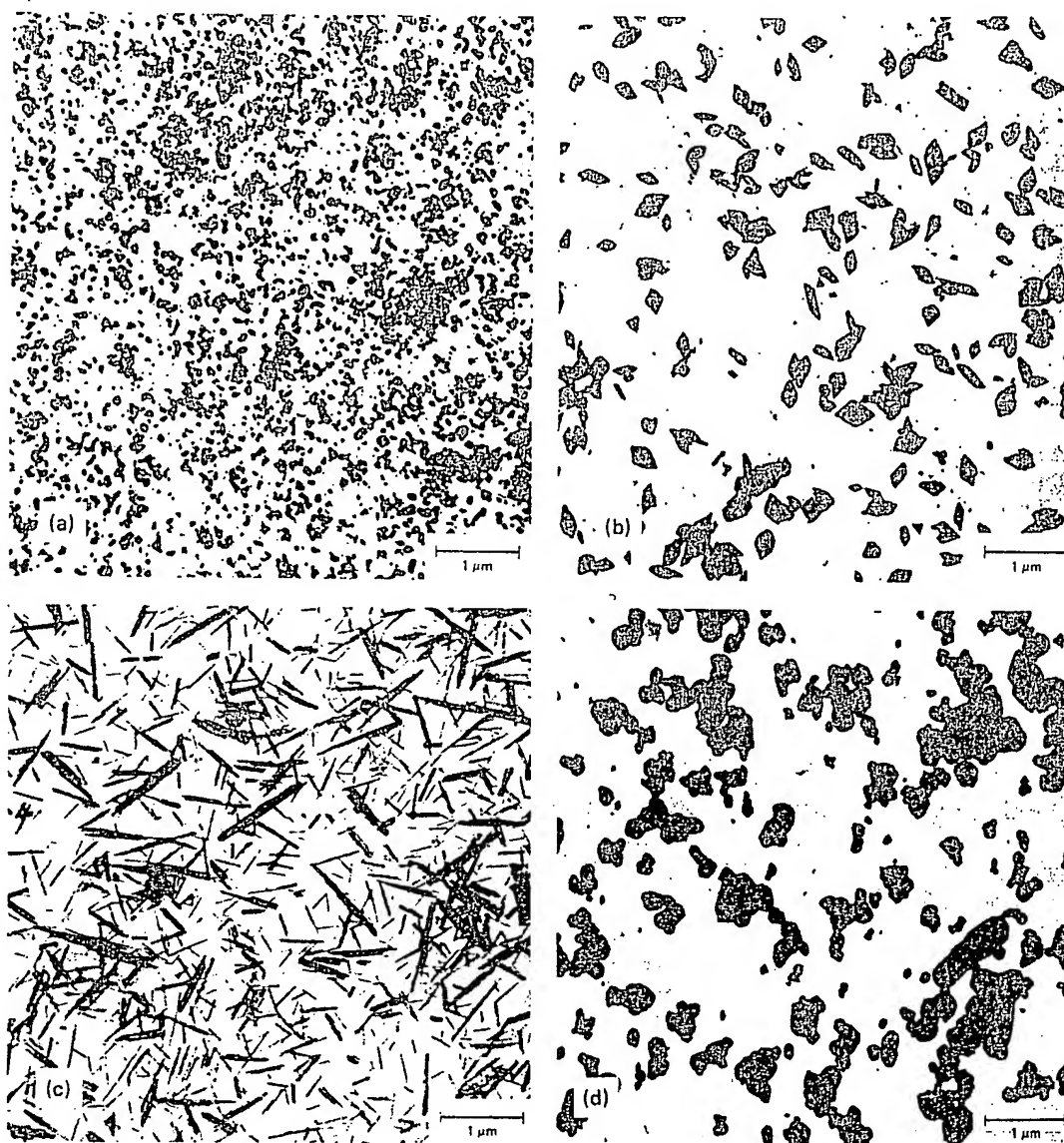
Figure 3. Electron photomicrographs of (a) Iron blue pigment. (b) Light (lemon) chrome yellow pigment. (c) Synthetic yellow iron oxide pigment. (d) Light red cadmium sulfoselenide pigment.

for hydrophobic pigments. In the case of hydrophilic pigments, a surfactant often is used to facilitate transfer from the aqueous to the nonaqueous phase. One drawback of flushing is that it limits the use of the pigment to application systems that are compatible with the vehicle used in the flushing.

Other pigments are prepared by calcination or by a combination of precipitation and calcination. Filtration, washing, drying, and grinding also are included in such processing. Calcinations involve heating materials to as high as 1000°C. The type of furnace, the temperature and length of time of calcination, and the type of atmosphere present during calcination, either oxidizing, reducing, or inert, are factors that affect the final pigment properties. Sintering of the pigment particles creates problems in dispersion and, therefore, is avoided. Another method of pigment manufacture is by vapor-phase reaction, eg, in the preparation of TiO_2 from $TiCl_4$.

Table 3.   Surface Area of Some Inorganic Pigments as Determined by Low Temperature Gas Absorption[a]

Pigment	Specific surface area, m²/g pigment
red lead	0.4
basic silica sulfate	0.8
chrome orange	1.28
zinc oxide	3.27
cupric oxide	3.4
chrome yellow	3.44
blanc fixe	3.79
ferric oxide	6.7
monobasic lead silicate	8.0
titanium dioxide	10.63
chrome green	13.60
iron blue	75
carbon black	117
synthetic silica	150

[a] Refs. 12–13.

Often, batch processes are used in pigment manufacture. However, numerous operations have been made more continuous with updated equipment and handling.

The most commonly sold pigment form is as dry solid in 23- and 45-kg bags. Bulk handling of dry pigment using air-bag systems also is employed. Pigments also are sold as presscakes, aqueous dispersions, color concentrates, slurries, and flushed colors.

Economic Aspects

In 1977 in the United States, there were 105 inorganic-pigment manufacturers who produced 1.27×10^9 worth of shipped product. Consumption by various industries of these pigments in 1977 was as follows: coatings and paints, >50%; paper, 20%; plastics, 10%; rubber, 3%; ceramics, 2%; the remainder went to miscellaneous outlets using colorants (14). A sampling of recent prices of pigments and extenders is tabulated in Table 4. Prices in recent years reflect increased costs of raw materials, fuels, labor, and transportation. There are also added costs of manufacturing because of equipment for pollution control in order to be in compliance with Federal and state governmental regulations.

Examples of reformulated colorants being marketed to offset soaring raw materials costs, in this case the cost of cobalt, and their 1981 retail prices are cobalt–lithium pigments, eg, V-9229 CoLiBlue [68186-85-6] at $15.54/kg and V-11649 CoLiGreen [68186-85-6] at $15.65/kg (16). Other new formulations include nickel complexes, transparent iron oxides, and high heat-stable phthalocyanine and nonflocculating blues.

A number of inorganic pigments is imported, some to supplement U.S. production, others because they are no longer produced in the United States. Certain natural pigments that are imported are not native to the United States. The value of imports relative to exports has increased over the last several years from a ratio of 1.5 to 3.0. Some statistics on imported inorganic pigments are listed in Table 5.

Table 4.   Prices of Inorganic Pigments and Extenders, October 1980[a]

Pigment or extender	$/kg
aluminum nonleafing paste, extra fine	3.53
antimony oxide	3.97
blanc fixe, direct process	0.474
cadmium red, concentrate	19.03–21.25
cadmium selenide lithopone, orange	7.12–8.16
calcium carbonate, water-ground, natural	0.047
carbon black, automotive, enamel-grade	3.35–5.60
chromium oxide	3.53
clay, delaminated	0.16
copper oxide	2.84–2.89
diatomite	0.055
iron blue	2.38
iron oxide	
red, domestic primer, natural	0.49–0.64
yellow, synthetic	1.047
lead chrome, yellow	2.69
mica	0.276
molybdate orange	3.04
sienna, Italian	1.28
silica	
amorphous	0.033
colloidal	1.46–1.85
talc, fine	0.17
titanium dioxide	
anatase	1.17
rutile	1.39
ultramarine	1.32
umber, Turkish	0.64
vermilion, English	18.58
zinc oxide, American process, lead-free	1.02

[a] Ref. 15.

The following are worldwide production statistics for 1978: titanium dioxide, ca 2.5×10^6 metric tons (83% of production); iron oxide pigments, ca 4.65×10^5 t (15%); chrome oxide pigments, ca 3.5×10^4 t (1.2%); cadmium pigments, ca 8500 t (0.3%); and mixed pigments, ca 8000 t (0.3%). In Western Europe, 64% of the titanium dioxide produced was used for coatings and 19% for plastics; 29% of the iron oxide was applied in coatings and 60% in building-material applications; 80% of the cadmium production was used in plastics, 10% in coatings and 10% for ceramics; and 50% of the chrome oxide pigments produced was incorporated in coatings, 25% in building materials, 10% in plastics and 10% in ceramics. The estimated value of U.S. inorganic pigment shipments during 1980 was 1.8×10^9 (14).

Health and Safety Factors

In manufacturing plants where known toxic substances are used, various handling techniques and safety measures are observed to protect workers against inhalation of fine particulate matter and injurious fumes, and against skin contact with chemicals.

Table 5. A Few of the Inorganic Pigments Imported by the U.S. During 1979[a]

Pigment	No. countries exporting to the United States	Metric tons
barium sulfate (barytes), natural	19	615
blanc fixe (pptd BaSO₄)	10	8,484
chalk, whiting	9	31,111
calcium carbonate (pptd)	6	8,137
chrome green	2	36
chrome oxide green	8	2,602
chrome yellow	6	1,241
cuprous oxide	4	251
iron blues	5	2,091
iron oxides, natural		
siennas	3	421
umbers	4	6,865
ochers	2	3
others	10	1,292
iron oxides, synthetic		
black	9	8,563
red	10	7,392
yellow	9	11,016
others	10	13,962
lithopone		
<30% wt ZnS	2	1,360
>30% wt ZnS	3	34
molybdate orange	1	373
titanium dioxide	18	95,277
ultramarine blues	8	2,802
Van Dyke brown	2	724
zinc oxide	10	26,907
zinc sulfide	4	741

[a] Ref. 17.

The regulatory agencies involved are EPA and OSHA (see Regulatory Agencies). Pigment usage near food is regulated by the FDA; other consumer products are controlled by the CPSC.

Threshold limit values for chemical substances and physical agents in the workroom environment are listed in ref. 18. Pigments listed as nuisance dusts are calcium carbonate, kaolin, titanium dioxide, and zinc dust and recommended TLVs for these are 10 mg/m^3 total dust or 5 mg/m^3 respirable dust. Some substances are listed as possible carcinogens, eg, lead and zinc chromates. An epidemiological survey of English workers at chromate pigment plants suggests that such workers are not exposed to greater risk for contracting lung cancer than nonworkers (19). Safety controls introduced for zinc yellow production apparently eliminate the potential carcinogenic effect of the chromate. Cadmium pigments, based on available information, seem to pose no known health problems (20). The effects of talc and its associated minerals are described in ref. 21. Pure talc apparently does not pose a serious problem. However, inhalation of large amounts of talc associated with certain asbestos minerals has produced higher than normal incidences of lung cancer and pneumoconiosis.

White Pigments

The principal white hiding pigment is titanium dioxide. Other white hiding pigments are zinc oxide, zinc sulfide, lithopone, and lead pigments, eg, basic lead carbonate, basic lead sulfate, and antimony oxide. Two principal sources of their opacifying properties in pigment applications are the difference between their refractive indexes as compared with those of the medium in which they are dispersed, and their small particle sizes which strongly influence light-scattering properties. Refractive index values and particle-size data are listed in Table 6. The best hiding power is displayed by rutile titanium dioxide, which opacifies better than the anatase form, and which hides nearly 7 times better than zinc oxide or antimony oxide, and 10 and 12 times better than basic lead carbonate and basic silicate white lead, respectively. However, the other white hiding pigments are used because titanium dioxide pigments, including those grades which are surface-treated, lack certain properties. For example, lead and zinc pigments react with oleoresinous vehicles and other acidic binders, forming soaps which improve flexibility of the paint film.

Shipments in 1977 of white opaque pigments, excluding TiO_2, were valued at $174 $\times 10^6$ (22). White lead, basic carbonate, and basic sulfate, excluding white lead in oil, contributed 9.4×10^6. Shipments of zinc oxide pigments were 179,300 t and were valued at 149×10^6. The value of all other white opaque pigments, including antimony oxide, lithopone, and pure zinc sulfide, was 16×10^6.

Titanium Dioxide. *Properties.* The stable crystal form is rutile; however, anatase can be converted to rutile at ca 700–950°C. Typical pigment properties of anatase and rutile TiO_2 are compared in Table 7.

Table 6. Characteristics of Some White Hiding Pigments

Pigment	Chemical composition	Refractive index[a]	Average particle size, μm
titanium dioxide, anatase	TiO_2	2.55	0.2
titanium dioxide, rutile	TiO_2	2.70	0.2–0.3
zinc oxide	ZnO	2.01	0.2–0.35
zinc sulfide	ZnS	2.37	0.2–0.3
lithopone	28% ZnS, 72% $BaSO_4$	1.84	0.2–0.3
lead carbonate, basic white lead	$2PbCO_3.Pb(OH)_2$	2.0	1.0
lead sulfate, basic	$PbSO_4.PbO$	1.93–2.02	0.8
antimony oxide	Sb_2O_3	2.1	1.0

[a] A common refractive index for a paint vehicle is 1.6.

Table 7. Typical Pigment Properties of Anatase and Rutile TiO_2

|	Anatase	Rutile
density, g/cm³	3.8–4.1	3.9–4.2
refractive index	2.55	2.76
oil absorption, g oil/100 g pigment	18–30	16–48
tinting strength, Reynolds method	1200–1300	1650–1900
particle size (av), μm	0.3	0.2–0.3

Titanium dioxide, mp >1800°C, is insoluble in water, organic solvents, alkalies, and most acids. It is attacked by sulfuric and hydrofluoric acids after long contact and high temperature. Radiant energy removes immeasurably small amounts of oxygen from titanium dioxide, even at room temperature, and affects the electrical and optical properties of the pigment.

An ideal white must reflect all wavelengths of visible light equally. Titanium dioxides do not fulfill this requirement completely because they absorb light below 430 nm in the far blue or violet end of the visible spectrum. In this region, the rutile form is more absorptive than anatase and displays a yellow tone which can be neutralized by decreasing the particle size of the pigment (23). Titanium dioxide pigments strongly absorb uv light, which results in the formation of excited species that oxidize organic molecules associated with the titanium dioxide in paint films and, thereby, catalyze the degradation of the finish. Reduction of this photoactivity has led to the modification of the titanium dioxide surface by means of specific surface treatments.

Manufacture.   Two processes have been commercialized for the manufacture of TiO_2; the older sulfate process and the chloride process which was developed during the 1950s. The prime consideration in developing new capacity is the availability and cost of raw materials, ie, of the more abundant ilmenite used in the sulfate process relative to the less abundant rutile required in the chloride process. A comparison of raw material requirements for TiO_2 pigment production is shown in Table 8. Another economic consideration is the effect of each process on the environment, with the chloride process producing much less waste material. Spent waste solutions from plants based on either process are neutralized with lime or limestone which provides an acceptable effluent for discharge to streams. Some of the neutralized waste by-products, gypsum, and iron oxides, are sold. Detailed economic aspects of TiO_2 pigments are given in ref. 24.

Sulfate Process.   The raw material source for the sulfate process is ilmenite ore, $FeTiO_3$ or $FeO.TiO_2$, or titanium slag. The TiO_2 content in ilmenite is 45–70 wt %. The ore is ground and then dissolved in concentrated sulfuric acid:

$$TiO_2.FeO + 2 H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + 2 H_2O \qquad (1)$$
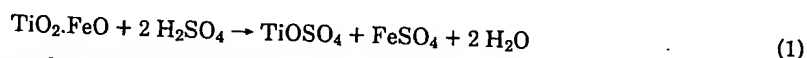
Iron is added to reduce the Fe(III) to Fe(II), and some titanium is reduced to prevent reoxidation of the iron. The solution is clarified, filtered, and concentrated by evap-

Table 8.   Material Requirements for Titanium Pigment Production[a], t Material/t Pigment

| Process and material	
sulfate process	
ilmenite or titanium slag	1.6–2.6
sulfuric acid	3–4
scrap iron	0.1–0.2
chloride process	
rutile	1.1–1.2
chlorine	0.1–0.2
petroleum coke	0.1–0.2
oxygen	0.4–0.5

[a] Ref. 25.

oration and the crystallized ferrous sulfate is separated and marketed as copperas [7720-78-7], a raw material used in the manufacture of iron oxide and iron blue pigments.

The titanium sulfate solution is hydrolyzed. Introduction of seed, ie, nucleating particles, prior to hydrolysis ensures that rutile is produced, whereas hydrolysis without the rutile nuclei results in formation of anatase titanium dioxide. The precipitate is separated from the solution by filtration and is washed. Additives are included to promote and control pigmentary characteristics in subsequent operations. The treated precipitated hydrate is calcined at 800–1000°C. Following calcination, the pigment may be ground or treated further with inorganic oxides to improve performance properties, eg, chalking resistance, dispersibility, and hiding power.

Chloride Process. Natural rutile used to be the only raw material used in the chloride process; however, ilmenite and other titanium ores can be used as source ores. A mix of the ore and coke is made which reacts with chlorine at 900°C, resulting in the formation of titanium tetrachloride, carbon dioxide, and carbon monoxide. Commercial chloride-process plants in the United States use fluid-bed chlorinators.

$$TiO_2 + C + 2\,Cl_2 \rightarrow TiCl_4 + CO_2 \qquad (2)$$
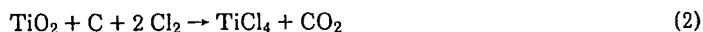
The titanium tetrachloride is separated from impurities, which can affect the brightness, by distillation. It then reacts with oxygen or air in a flame reaction at ca 1500°C to produce chlorine and fine-particle titanium dioxide; the former is recycled.

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2\,Cl_2 \qquad (3)$$
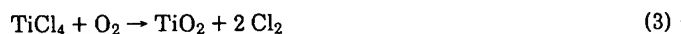
Aluminum trichloride is added to promote production of the rutile form and to correct crystal size.

The TiO_2 can be posttreated to improve pigmentary properties, eg, photochemical stability. Posttreatments include application of inorganic oxides and other compounds to the surface. Coatings of 2–5 wt % alumina or alumina and silica are satisfactory for general-purpose paints. If greater resistance to weathering is desired, the pigment is more heavily coated to ca 7–10 wt %. The coating can consist of a combination of several materials, eg, alumina, silica, zirconia, aluminum phosphate, or phosphates of other metals (26).

Six companies produce titanium dioxide pigments in the United States. Rated capacities for these plants for 1977 totaled 8.29×10^5 metric tons per year of which 5.69×10^5 t was produced by the chloride process (27). Approximately 6.4×10^5 t TiO_2, of which 2.4% was exported, was shipped in 1977. U.S. production of TiO_2 in 1980 was ca 7.2×10^5 t.

Uses. The following are domestic applications: 52% in paint, varnish, and lacquer; 20.7% in paper; 11.7% in plastics (except floor covering and vinyl-coated fabrics and textiles); 3.1% in rubber; 1.9% in ceramics; and 8.2% in printing ink and other applications (28). Titanium dioxide provides whiteness, brightness, and opacity in paints. In paper coatings and as a paper filler pigment, it improves printability. Its chemical inertness and resistance to degradation by uv light provides a large market for TiO_2 in plastic materials, eg, polyethylene, poly(vinyl chloride), polystyrene, and polyolefins.

Zinc Oxide. Zinc oxide has a density of 5.6 g/cm^3 and displays oil-absorption values of 10–25 g/100 g. Syntheses for pigmentary zinc oxide were developed in France and in the United States in the 1830s. Most of the zinc oxide produced today is manufactured by two methods which are based primarily on sphalerite, ZnS, as the starting ore. The French process is indirect; the first step is vaporization of zinc metal followed by its oxidation, and collection of the zinc oxide powder. The U.S. process is more direct and is based on the development of a cast-iron grate, the Wetherill grate, which makes possible the burning of a charge of zinc sinter and coal in a furnace and the conversion of the resulting zinc vapor to zinc oxide. Several types of furnaces are employed in the two processes.

The various grades of zinc oxide produced from each process are dependent on the purity of the zinc oxide, the particle size, and particle shape. Impurities left in zinc oxide from the French process are metallic oxides and sulfur, whereas impurities from the U.S. process are metal sulfates. Zinc oxide is labeled lead-free if the minimum ZnO content is 98 wt % by the U.S. process or 99 wt % by the French process. The U.S. process results in particle shapes from nodular to coarse acicular and the shape depends on the length of the cooling stage during manufacture; rapid cooling produces round particles.

The largest consumer of zinc oxide is the rubber industry in which zinc oxide is used with sulfur and organic accelerators to cure elastomers by vulcanization. Approximately 7% of the total amount of zinc oxide shipped in 1977 was used by the paint industry (29). Its use in paints is based on properties other than hiding power. Zinc oxide absorbs uv radiation and, thereby, protects organic binders from photodegradation and reduces chalking. Because zinc oxide acts as a fungistat, it is used in exterior oil paints. The tendency to form zinc soaps with oleoresinous vehicles can be controlled to some extent with acicular-type zinc oxide and formulation modification.

Zinc oxide is being used increasingly in photocopying as well as in textiles, lubricants, pharmaceuticals (qv), floor coverings, and ceramics, eg, glass, glazes, and enamels, and improves magnetic properties of ferrites (qv) (see Electrophotography; Textiles; Colorants for ceramics; Colorants for foods, drugs, and cosmetics).

Leaded Zinc Oxide. Densities of and oil-absorption values for leaded zinc oxides are 5.21–6.0 g/cm^3 and 11–16 g/100 g, respectively.

There is a small demand for leaded zinc oxide, which can be prepared either by co-fuming lead and zinc ores, or by physically blending lead-free zinc oxide and basic lead sulfate or basic lead silicate. Leaded zinc oxide products commonly contain 12–55 wt % basic lead sulfate.

Zinc Sulfide. Zinc sulfide is no longer manufactured in the United States but is imported from the FRG. Its refractive index, density, and oil-absorption values are 2.37, 4.0 g/cm^3, and 13 g/100 g, respectively. It is a softer pigment than TiO_2, and possesses a Mohs hardness of 3.5–4.0 compared to 5–7 for some grades of titanium dioxide pigments. Zinc sulfide does not exhibit the yellowish undertone associated with TiO_2 and is useful where a purer and cleaner white is required. Zinc sulfide absorbs less uv light than titanium dioxide and, therefore, is a better optical brightener and is used in space-vehicle finishes.

Pure ZnS was produced in Europe and in the United States during the 1920s and was the result of gradual replacement of a lithopone product which contained 30–60 wt % ZnS and the balance $BaSO_4$. After World War II there was a gradual decline in the use of ZnS in favor of TiO_2.

Zinc sulfide is produced by the reaction of $ZnSO_4$ with Na_2S to yield ZnS and Na_2SO_4. Impurity removal from the $ZnSO_4$ is essential to obtain high brightness and whiteness. The precipitated ZnS is filtered by rotary filters, dried, and calcined at 650°C to produce material with an average particle size of 0.3 μm.

Lithopone. Lithopone is a mixed pigment which originally consisted of 28–30 wt % ZnS and 70–72 wt % $BaSO_4$. Grades with higher, ca 60 wt %, zinc sulfide contents have been developed. Use of lithopone, particularly in the United States, has declined since the introduction of titanium dioxide.

Lithopone is prepared by coprecipitation of ZnS and $BaSO_4$:

$$ZnSO_4 + BaS \rightarrow ZnS + BaSO_4 \tag{4}$$

To increase the ZnS content, $ZnCl_2$ is introduced as a reactant producing $BaCl_2$ with ZnS and $BaSO_4$.

Lithopones are used in water-base paints because of their excellent alkali resistance, in paper manufacture as a filler and opacifying pigment, and in rubber and plastics as a whitener and reinforcing agent.

Basic Lead Carbonate. White lead was a pigment widely in use in ancient times and is considered the oldest of the white hiding pigments. Todays' usage is limited because of the growth of titanium dioxide and restrictions on the use of lead components in products like paint.

White lead is composed of basic lead carbonates, the principal chemical component is $2PbCO_3 \cdot Pb(OH)_2$. Pigment particles possess hexagonal outlines with the higher basicity type supposedly a more flaky, more irregularly shaped, and appreciably finer particle than $2PbCO_3 \cdot Pb(OH)_2$. The basic lead carbonates are finer than normal lead carbonate, which is not considered a good pigment. Density and oil absorption values for basic lead carbonates are 6.75–6.95 g/cm^3 and 11–25 g oil/100 g pigment, respectively.

Most basic lead carbonate is manufactured by one of three processes: the H.T.S. Carter process, the combination Carter-tank finishing process, and a straight precipitation process (30). The Carter-tank finishing procedure requires about three days for manufacture of white lead. A lead oxide is charged to slowly revolving cylinders and is moistened and sprayed with acetic acid. Carbon dioxide is introduced and reacts with the contents of the cylinder to form basic lead carbonate. Carbonation is completed in large tanks where the charge from the cylinders is pumped after having been disintegrated and classified.

The most practical tank precipitation procedure is the Thompson-Stewart process. Litharge, the raw material for the process, is contained in a water slurry with catalytic amounts of acetic acid. Any free lead present in the litharge is oxidized prior to carbonation with flue gas.
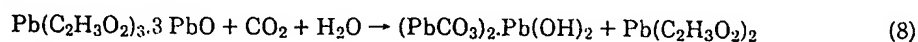
The chemical reactions for all the processes are similar:

$$2\,Pb + O_2 \xrightarrow{\text{moisture}} 2\,PbO \tag{5}$$

$$PbO + 2\,HC_2H_3O_2 \rightarrow Pb(C_2H_3O_2)_2 + H_2O \tag{6}$$
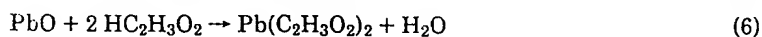
Acetic acid is present in small amounts, and the excess litharge reacts with the lead acetate:

$$Pb(C_2H_3O_2)_2 + 3\,PbO \rightarrow Pb(C_2H_3O_2)_2 \cdot 3\,PbO \tag{7}$$
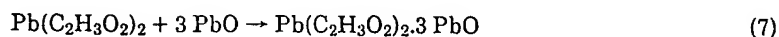
The final step is carbonation.

$$Pb(C_2H_3O_2)_3 \cdot 3\,PbO + CO_2 + H_2O \rightarrow (PbCO_3)_2 \cdot Pb(OH)_2 + Pb(C_2H_3O_2)_2 \tag{8}$$

The H.T.S. Carter process results in a white lead with a carbonate content that is up to 5 wt % higher than from the precipitated process, which results in $PbCO_3$ contents of 62–64 wt %. Basic PbO content for the product of the precipitated process is ca 37 wt %, ie, ca 3% higher than the basic PbO content for the H.T.S. Carter process. White leads with lower carbonate contents are finer-sized pigments and are characterized by higher tinting strengths and better overall paint properties.

Applications of basic lead carbonate are limited. It is less reactive than zinc oxide and, since it is basic and a good acid acceptor, it is used in corrosion-resistant paints. White lead imparts adhesion and toughness to paint film, thereby improving durability. Drawbacks are lead toxicity and poor chemical resistance to sulfide-laden industrial atmospheres. White lead is used as a stabilizer for poly(vinyl chloride); it retards the rate of degradation by heat and light by means of its reaction with hydrogen chloride. Basic lead carbonate is sold as a dry pigment or as a paste in linseed oil or as a semipaste in oil.

Basic Lead Sulfates. Typical density and oil absorption values for basic lead sulfate are 6.4 g/cm^3, and 8 g/100 g, respectively. White basic lead sulfate can be manufactured by a fume process. Atomized molten lead is combined with sulfur dioxide in the presence of air and the lead sulfate fume is cooled and collected. It also can be prepared by roasting galena, PbS. The chemical formula for basic lead sulfate is variable, owing to the fact that several basic salts can be formed, but it generally is represented as $PbSO_4.PbO$, with the marketed pigment containing 15–20 wt % PbO.

A precipitation process can provide monobasic lead sulfate, $PbSO_4.PbO$, along with lead sulfates of higher basicity, eg, tribasic lead sulfate [12397-06-7], $PbSO_4.3PbO$.

Uses. Basic lead sulfate imparts the same properties as basic lead carbonate, eg, adhesion, durability, acid acceptance, and rust inhibition, but is somewhat less effective. White basic lead sulfate is characterized by low basicity and, therefore, low reactivity and is used in combination with zinc oxide at ca 35 wt %. High basicity lead sulfates are used to stabilize vinyls and other plastics (see Heat stabilizers).

Blue basic lead sulfate is marketed as a metal-protective pigment; however, its use is declining. It consists of 78 wt % monobasic lead sulfate, 10 wt % lead sulfide, 4 wt % lead sulfite, 4 wt % zinc oxide, and 4 wt % carbon and other materials. The carbon imparts the blue color.

Basic Lead Silicate. The composition $3PbO.2SiO_2.H_2O$ approximates the formula of basic lead silicate pigment. The low silica type has a density of $6.4/cm^3$ and an oil absorption of 16 g/100 g, whereas the respective values of the high silica type are 4.0 g/cm^3 and 13 g/100 g. Lead silicates are characterized by low tinting strength and low hiding power but have many similar properties to white lead. Two grades are marketed; one product contains 48 wt % PbO and the other, 84 wt % PbO.

Basic Lead Silicosulfate. Basic lead silicosulfate was the first of a group of coated silica-cored pigments and was introduced to the market in 1948. The coating around the silica core consists of a mixture of gamma tribasic lead silicate and monobasic lead sulfate. Pigment manufacturing involves the reaction of slurries of litharge and silica which contain acetic acid catalyst. Sulfuric acid is the source of sulfur trioxide. The filtered slurry is calcined and the typical chemical composition of the pigment product is 47.9 wt % PbO, 47.9 wt % SiO_2, and 4.2 wt % SO_3. The density is 4.9 g/cm^3. Silicate provides film durability properties and the lead sulfate component stabilizes the whiteness of the lead silicate. Approximately 38% less pigment is nec-

essary for the basic lead silico sulfate formulation, as compared to that for white lead and basic lead sulfate, and durability is not compromised. Two reasons for its use are reduced costs and, in latex primers, the reduction of bleeding from woods, eg, redwood and cedar.

Dibasic Lead Phosphite. Dibasic lead phosphite was first marketed in 1950 and is used in plastics and in light or pastel-colored anticorrosion primers and paints (31) (see Colorants for plastics). It has a density of 6.67 g/cm^3 and an oil-absorption value of 14 g/100 g.

Antimony Oxide. Antimony oxide has a density of 5.3–5.7 g/cm^3 and an oil absorption of 11–14 g/100 g.

In the presence of a halogen, eg, chlorine, antimony oxide, Sb_2O_3, becomes an effective fire retardant in paint, plastics, and textiles (see Flame retardants). The initial growth of Sb_2O_3 as a pigment resulted from its control of chalking and the consequent improvement of tint retention in exterior enamels, eg, automotive and house paints. The introduction of pure rutile titanium dioxide in 1941, which was characterized by similar properties in addition to better hiding power, led to the decline of antimony oxide for this use.

Antimony oxide can be prepared by roasting stibnite, Sb_2S_3,

$$2\,Sb_2S_3 + 9\,O_2 \rightarrow 2\,Sb_2O_3 + 6\,SO_2 \tag{9}$$
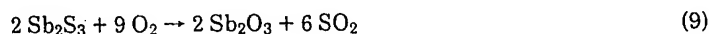
or by vapor oxidation of the metal.

$$4\,Sb + 3\,O_2 \rightarrow 2\,Sb_2O_3 \tag{10}$$

Antimony oxide promotes curing of finishes applied to steel coils. It also is used in the manufacture of ceramics, vitreous enamels, and as a decolorizer in glass.

Zirconium Oxide and Zircon. The indexes of refraction for zirconium oxide and zircon, ie, zirconium silicate, are 2.1–2.2 and 2.0, respectively. Because suitable pigmentary sizes cannot be manufactured commercially, they are not used in such commercial items as paints, plastics, rubber, and inks. However, these crystalline pigment opacifiers are used in porcelain or vitreous enamels. Zircon and zirconium oxide serve as host crystal lattices for foreign metallic ions. For example, vanadium-doped zircon is a blue pigment used in the glaze and enamel industry. Vanadium-doped zirconium oxide results in a yellow stain (32).

Extender Pigments

Extender pigments are low cost, generally colorless or white pigments with refractive indexes less than 1.7. Many extenders are derived from natural sources and they display many diverse properties. In coating applications, extender pigments control gloss, viscosity, texture, suspension, and durability and they enhance the opacity of white hiding pigments, eg, TiO_2. In plastic applications, extenders influence numerous properties of the resin, including melt viscosity, improve thermal conductivity and electrical properties, change tensile strength, and improve moisture resistance. Some natural and synthetic extender pigments are compared in Table 9.

Clay or Kaolin. Kaolin is a hydrous aluminosilicate mineral with principal deposits mined in Georgia, South Carolina, and Texas. Kaolins are characterized by the following chemical analyses: aluminum oxide, 38.5 wt %; silicon dioxide, 45.5 wt %; combined water, 13.9 wt %; titanium dioxide, 1.5 wt %; and percentages of calcium

Table 9.   Properties of Some Extender Pigments

Pigment	Chemical composition	Refractive index	Particle size, μm
hydrated aluminum oxide	$Al(OH)_3$	1.57	0.4–8
barium sulfate, natural	$BaSO_4$	1.64	2–5
blanc fixe, synthetic	$BaSO_4$	1.64–1.65	0.5–2
calcium carbonate			
natural	$CaCO_3$	1.49–1.66	1–200
synthetic	$CaCO_3$	1.49–1.66	0.03–10
calcium silicate, natural	48% CaO, 52% SiO_2	1.62	1–5
clay (kaolin)	hydrous aluminum silicate: 38.5 wt % Al_2O_3, 45.5 wt % SiO_2	1.56	0.5–3.5
silica			
diatomaceous	fossilized silicous remains of diatoms	1.42–1.48	4–12
synthetic	95–99% SiO_2	1.50	0.02–0.11
talc	hydrous magnesium silicate	1.54–1.59	2–9

oxide, magnesium oxide, iron oxide, and others, <1.0 wt %. A single crystal of kaolin consists of a layer of silica that is chemically bonded to a layer of hydrous alumina (see Clays).

Clays are graded according to size, ie, fine, intermediate, and coarse. Particle sizes of the fine clays are 0.2–0.8 μm. The finest particle size clays have surface areas of ca 20 m^2/g and oil-absorption values of 45 g/100 g. The typical particle size and surface area of intermediate grades are 1.5 μm and 8 m^2/g, respectively. Particle sizes and surface areas of coarse clays are 5–10 μm and 5–7 m^2/g, respectively. The latter grade displays oil-absorption values of 30–40 g/100 g. Typical density and hardness values of kaolins are 2.58 g/cm^3 and 2.5 Mohs, respectively. The calcined varieties have a slightly higher density, ie, 2.63 g/cm^3, and possess a higher oil-absorption value, ca 55 g/100 g.

Mined clay is slurried at the open-pit mine site and the slurry is pumped to de-gritting equipment and then stored in tanks for further processing. Slurries are blended, and control of particle size distribution is maintained throughout processing. Centrifugal classification of the clay suspension separates the clay particles into two fractions: one fraction contains thin, flat hexagonal plates <2-μm dia; the other fraction, with particles larger than 2-μm dia, consists of stacks of these hexagonal plates. Clay slurries are decolorized by a chemical leaching process and by magnetically separating iron contaminants. The clay particles are removed from suspension using press filters, rotary filters, or continuous centrifuges. The plastic clay cake is dried in apron dryers or reslurried and spray-dried.

Kaolin is processed further to improve properties, eg, brightness and dispersibility, as well as electrical properties, and water resistance. Mechanical delamination can break down the stacks of clay platelets and produces a delaminated clay with increased hiding power. Whiteness is improved by calcining the kaolin at 1000°C or higher in rotary kilns which causes evaporation of the water of crystallization and alters the structure. Calcined clay provides adequate filler properties for use in plastic compounds. Clays also may be surface-treated.

The paper and paperboard industry use kaolin as a filler, and it is a principal pigment in paper coatings. Kaolin extends titanium dioxide in paint and promotes film integrity, covering power, durability, flow and leveling, and gloss control. Calcined kaolins are white and hard; they are used in traffic and water-based paints. Kaolin also is used in ceramics, rubber, thermoset plastics, and adhesives.

Attapulgus Clay. Attapulgus clay [1337-76-4] is a crystalline hydrated magnesium aluminum silicate and a member of a group of sorptive clays called Fuller's earth. Attapulgus clay consists of three-dimensional chains and, with proper cleavage of the crystal structure, yields a high surface-area porous clay. It is used in paints as a flattening agent and in sealants as a bodying-control agent.

Calcium Carbonates. Natural calcium carbonates are quarried or mined. Limestone is any rock containing more than 50 wt % calcium carbonate, usually the calcite form. The rest consists of impurities, mainly dolomite with lesser amounts of clay, carbon, quartz, iron, and manganese compounds. Several types of limestones are available, eg, crystalline limestones, in which the calcium carbonate is calcite; marble; and chalk, which is composed of shells of one-celled animals called Foraminifera. After being mined, the minerals are crushed and ground (see Lime and limestone).

Various wet or dry grinding methods are used including ball, tube, and roller mills. Classification of the ground calcium carbonate can be by levigation or air classification. Further grinding by means of fluid-energy mills, ie, jet mills or micronizers, prepares the various marketed grades.

Natural calcite has a density of 2.71 g/cm^3, particle sizes are 1.5–12 μm, and oil-absorption values are 6–15 g/100 g.

Limestone is the raw material used in the manufacture of precipitated grades of calcium carbonate. The limestone first is calcined in kilns and the resulting calcium oxide or quicklime is slaked with water to form calcium hydroxide. In the recarbonation process, $Ca(OH)_2$ reacts with CO_2 and the reaction temperature and raw material concentrations are controlled to maintain specific particle size and shape. The product is the aragonite form of $CaCO_3$ with average particle sizes of 0.2–2.0 μm. In a second process, the $Ca(OH)_2$ reacts with Na_2CO_3 to form $CaCO_3$ and NaOH. Efficiency of sodium hydroxide recovery determines the particle size of the calcium carbonate. Greater recovery is realized with coarse particles; with fine-particle production, the sodium hydroxide is more difficult to remove. Nonremoval causes formulation problems because of high pH values.

A third process is the calcium chloride process, by which a calcium chloride solution is prepared by reaction of calcium hydroxide with ammonium chloride. Following purification of the calcium chloride, calcium carbonate precipitates with sodium carbonate. This procedure is part of the Solvay process for preparing Na_2CO_3 from NH_3 and brine.

Synthetic calcium carbonates are available in many grades of two crystalline forms, ie, calcite and aragonite. Some grades are surface-treated with stearic acid or rosin to improve rheological properties. The extremely fine grades display poor dispersion properties. Good dispersibility is achieved with particle sizes of ≥0.15 μm. Specific gravities of calcite and aragonite forms of $CaCO_3$ are 2.6–2.75 and 2.93, respectively. Oil-absorption values vary from 28 g/100 g for a coarse calcite to 58 g/100 g for a very fine calcite. The precipitated forms generally contain ≥98.5 wt % $CaCO_3$ and exhibit high brightness.

Natural calcium carbonate or whiting is a widely used, high tonnage pigment.

The high calcium types are preferred over the dolomite types, which display low brightness, and are more reactive because of the magnesium content. These pigments are used in paints, plastics, rubber, paper, adhesives, and joint fillers. Exterior use is limited to white paint because of the formation of calcium sulfate from the reaction of whiting with acid rain.

The greatest demand for precipitated calcium carbonate is by the paper industry for filler and coatings. The next largest uses are in paints and plastics. The printing-ink industry uses calcium carbonate and, in particular, the ultrafine grades, for high quality letterpress and litho inks (see Fillers; Ink).

Barium Sulfate. Barium sulfate can be prepared synthetically or it can be obtained naturally from the mineral barite (baryte), which is referred to in commerce as barytes or heavy spar because of its specific gravity. The principal use of barite is as a weighting material in well-drilling muds; it aids in pressure suppression, thereby preventing blowouts. This one use accounted for 91% of the total U.S. consumption of nearly 2.4 $\times 10^6$ t in 1977 (33) (see Petroleum, drilling fluids). 3% of the 1977 consumption was for use as a filler and extender pigment in various industries. Barite contributes to the gloss in topcoats and automobile paints and it is a filler in primer coats. Barite is used in plastics for floor mats and in carpet backing with polyurethane foam. White sidewalls utilize barite in conjunction with zinc oxide. It acts as an oxidizer and decolorizer in glass and is used as a filler in papers.

Barite is an attractive extender pigment because of its chemical inertness, high refractive index in relation to other extender pigments, high specific gravity (4.5), low oil absorption (9 g/100 g), low abrasiveness, a Mohs hardness of 3.0, its wettability, and dispersibility. Processing of the mineral for pigment use involves wet grinding, levigation to size particles, and bleaching. Further size reduction can be achieved by jet milling and classification.

Blanc fixe, which is the precipitated form, is prepared by reaction of a soluble barium salt with a soluble sulfate. The finer particle of the synthetic compared to the natural barium sulfate allows its use in printing inks to effect transparency. Special grades, low in sulfide content, are prepared for photographic paper, pharmaceutical use, and for use as a special reflectance standard. Blanc fixe also is used in the preparation of other pigments, eg: lithopone ($ZnS/BaSO_4$), and cadmium lithopones ($CdS/BaSO_4$, $CdSe/BaSO_4$, etc).

Magnesium Silicate (Talc). Magnesium silicate is derived from natural sources which include talc, soapstone, steatite, asbestine, and others. The principal talc mining districts in the United States are in New York, Vermont, Montana, Nevada, and California. Commercial talc is available in many grades of variable composition, but the chemical composition is designated as $(MgO)_3.4SiO_2.H_2O$. Structurally pure talc is composed of a sheet of brucite ($MgO.H_2O$) which is sandwiched between two silica (SiO_2) sheets (34). These sheet layers are held together by weak forces that allow the layers to slide past one another, which accounts for the soft and slippery feeling of talc. Talcs vary in particle shape, depending on their source. They may be fibrous or acicular, platy or laminar, or they may be granular.

Magnesium silicate has a density of 2.7 g/cm³ and oil-absorption values are 30–50 g oil/100 g pigment. It has a Mohs hardness of one.

The fibrous types are characterized by high oil-absorption and, for some types, high surface area. They improve rheological properties, eg, reduce settling, reduce sagging, and give better brushability, in paints. Talcs aid in reducing checking, blis-

tering, and cracking of paint film, thereby increasing film durability. The laminar types are useful in undercoating systems. Improvement in corrosion and humidity resistance is gained by increasing the path length of moisture through the film. Talcs also possess excellent sanding properties and are used in primers and as reinforcing fillers in plastics. Other applications are in ceramics and cosmetics (see Talc).

Calcium Silicate. Natural calcium silicate is derived from wollastonite. The largest deposit of wollastonite intended for pigment use is in Willsboro, N.Y. It is acicular with a low to moderate oil absorption, a refractive index of 1.63, and a pH of 9.9 in a water slurry. Because of its alkalinity, it can be used as a buffer for latex paints. It also is used in plastics, sealants, wallboard, insulation, and elastomers.

Synthetic calcium silicate is prepared by a hydrothermal reaction involving diatomaceous silica and lime, which results in the formation of a hydrous calcium silicate, $CaO.SiO_2.nH_2O$. High surface area colloidal particles of varying particle shapes form. The use in coatings is primarily for water-thinned emulsion paints where good hiding is achieved by air voids. When calcium silicate is dispersed in a latex resin, the agglomerates, which are dry and consist of clusters of ultimate particles surrounding air pockets, are not totally wetted and the setting of the paint film by evaporation of the water enhances the opacity because of the trapped air. The high oil absorption of synthetic calcium silicate provides for efficient flattening effects.

Wollastonite has a density of 2.9 g/cm^3, an oil absorption of 25–30 g/100 g, and a Mohs hardness of 4.5. Two synthetic calcium silicates have refractive indexes of 1.55, densities of 2.26 and 2.41 g/cm^3, and oil-absorption values of 170 and 280 g/100 g, respectively.

Natural Silicas. *Amorphous.* Tripoli deposits in the United States are in Missouri, Illinois, Arkansas, and Oklahoma (see Silica, amorphous). Rottenstone, which is another form of tripoli, is mined in Pennsylvania. These silicas are not amorphous. The finest, whitest, softest grade of silica is obtained from mines near Cairo, Ill. Illinois silica is an extremely fine crystalline structure whose crystallinity is undetectable under microscopic examination and is termed cryptocrystalline. Pigment-grade silicas are 99 wt % SiO_2, and have refractive indexes of 1.54–1.55 and a specific gravity of 2.65. The tripolitic ores are mined, crushed, and pulverized. Grade classification is by water and air separation and the silica is jet-milled if it is to be used in high speed paint-grinding equipment.

The bulk of its use is as an abrasive, eg, buffing compounds and polishes, and fine grades are used for polishing optical lenses. Its application in paint is limited because of its texture, ie, it is difficult to disperse, abrasive, and poor in settling characteristics when improperly formulated. Because of its low cost and inertness, silica is used in paste wood fillers, undercoating, and flat paints because it provides easy brushing and improves the adhesion of the topcoat by the tooth effect. Silica is used for underfoot coatings, eg, in floor, deck, and traffic paints, to improve wear resistance and to provide an antislip surface. Other applications are in plastics, elastomers, toothpaste, and ceramics.

Crystalline. Commercial-grade deposits of quartzite are in Illinois, Missouri, New Jersey, Oklahoma, Pennsylvania, and West Virginia. The ore is crushed, foreign matter is removed in settling tanks, and the product is dried, pulverized, and classified. Particle sizes of available grades are <5 μm to >150 μm. The chemical inertness, extreme purity, typically 99.7 wt % SiO_2, and low cost of crystalline silica render it useful as a reinforcing filler for silicone rubber. It also is used in caulking compounds and improves porcelain insulator bodies.

Novaculite. Novaculite is obtained from quarries near Hot Springs, Arkansas. Pigment surface area is 2 m²/g for a mean particle size of 4.0 μm. The pigment has a refractive index of 1.55. It is used in plastics because it is less abrasive than other silicas. Other properties are good extrudability and good thermal and electrical characteristics.

Diatomaceous. Diatomaceous silica pigments are hydrous silica derived from natural origins. They essentially are the fossilized siliceous skeletal remains of single-cell aquatic organisms called diatoms. A myriad of shapes and forms showing complex patterns of lattice work are known. Pigment characteristics vary greatly because of the open, porous structure of the diatom skeleton. The natural color is gray, the calcined color is white, and the refractive indexes are 1.42–1.48. Surface areas are 3–15 m²/g. Oil absorption, by ASTM D 281-31, is 90–150 g/100 g.

Diatomaceous silica beds are worked by open or strip mining but, during processing, care is exercised so as to not crush and destroy the unique diatom structure. Typical chemical analysis for this pigment is 86 wt % SiO_2, 5 wt % Al_2O_3 and Fe_2O_3, and trace amounts of Na_2O, K_2O, CaO, MgO, P_2O_5, and TiO_2.

Diatomaceous silica controls gloss and sheen of flattening paints, water-thinned emulsion flat wall paints, flat varnishes, primers, and concrete and stucco finishes. When incorporated into plastic film, it imparts antiblocking characteristics and, thus, reduces the tendency of the film to stick together (see Abherents). Care must be taken to avoid excessive grinding which can result in more sheen, less film porosity, and lower paint consistency when the diatomite particles are reduced in size (see Diatomite).

Synthetic Silicas. *Precipitated.* Precipitated silicas are characterized by large surface areas, ca 100–300 m²/g; high oil absorption, >150 g/100 g; a refractive index of 1.46, and average particle sizes of <0.3 μm. A representative commercial product is Hi–Sil (PPG Industries).

Precipitated silica products have no counterpart in nature and do not bear any relationship to other synthetic silicas, eg, the fume and pyrogenic types or the silica gels. Much of the literature on the precipitated silicas is in patents. The manufacturing methods are batch processes involving growth by aggregation, continuous processes involving growth by aggregation, and processes involving mediation and subsequent growth by accretion of monomer (35). All involve the controlled treatment of a silicate solution with acid (see Silica).

Pyrogenic. Pyrogenic silicas are extremely pure SiO_2 and are prepared from high temperature reactions. Today's commercial processes involve burning of $SiCl_4$ with H_2 and O_2 at 1000°C. Because this process utilizes a homogeneous gas mixture, a narrow particle size distribution is obtained. Pyrogenic silica is amorphous to x rays and does not cause silicosis, but excessive inhalation should be avoided (36). Pyrogenic silica particles have surface silanol ($≥SiOH$) groups and internal Si–O–Si bonds. The silanol groups determine the silica's physical and chemical properties. Particle sizes are 3–10 nm with surface areas of 50–380 m²/g. Pyrogenic silicas are used in rubber and plastics. Cab–O–Sil (Cabot Corp.) and Aerosil (Degussa) are two commercial products.

Aerogel and Hydrogel. Aerogel and hydrogel silicas are characterized by surface areas 100–400 m²/g, high porosity, and a refractive index of 1.46. Their primary function in surface coatings is as a flattening agent. They display a desiccant effect and, therefore, improve package stability of paints containing metallic pigments by preventing hydrogen formation from a reaction of metallic flake and water. Silica

aerogels and hydrogels develop viscosity and thixotropic behavior in aqueous systems. Manufacturing technology is described in patent literature and is summarized in ref. 37.

Micas. Micas are complex aluminum potassium silicates and the mica of greatest commercial value is muscovite. Micas are characterized by unique platy particles with higher diameter-to-thickness ratios than any other flakelike mineral. Mica is characterized by a refractive index of 1.58, specific gravities of 2.5–2.8, oil-absorption values of 56–74 g/100 g, and a Mohs hardness of 2.5.

Selection for use is based on color, and processing involves wet or dry grinding of the mica to pigmentary size. During grinding, the large sheets of mica are delaminated. Particles are graded according to settling and floating techniques. The mica then is dewatered by centrifuging and the fines are classified, normally to 44–88 μm (325–170 mesh). Dry grinding is achieved by hammermilling or by grinding in attrition mills and is followed by mechanical screen classification. Fluid-energy mills and micronizer mills also are used.

Micas are used in wallpaper and coated paper, rubber, primer and anticorrosion coatings, other types of paint, joint cements, plastics, lubricants, greases, nacreous pigments, electrical insulation, and fire-proofing materials. Its platy structure reinforces films by increasing cracking resistance, it improves paint durability because of its high opacity to uv radiation and it promotes corrosion resistance by lengthening the path of moisture through the paint film (see Micas, natural and synthetic).

Others. Hydrated aluminum oxide is manufactured by seed nucleation of a saturated alumina solution. Hydrated aluminum oxides are fine, white pigments with a refractive index of 1.57. Hydrated aluminum oxides are characterized by high purity, high brightness, fire-retardant properties, and good dispersibility. They are used in numerous materials, eg, rubber, paints, inks, plastics, and paper. Improvement in hiding in paint systems is accomplished with titanium dioxide.

Light alumina hydrate is prepared by reaction of sodium carbonate and aluminum sulfate. The method of preparation varies the composition of basic aluminum sulfate. It finds use as a base in the preparation of lake pigments. Because of its high oil absorption, light alumina hydrate increases viscosity of lithographic inks, thereby improving the working properties of the ink. Its reactivity can be detrimental, especially where it is used with an acidic vehicle, as it causes livering, ie, solidification. Satin white is prepared by reaction between slaked lime and aluminum sulfate and the product contains a slight excess of lime. The empirical formula of the pigment is $3CaO.Al_2O_3$-.$3CaSO_4.32H_2O$. It is used principally in coated paper. Gloss white is a composite pigment containing 75 wt % blanc fixe and 25 wt % aluminum hydrate and it is used in printing inks. Pumice is a glossy, volcanic lava composed mainly of complex silicates of aluminum, calcium, magnesium, iron, potassium, and sodium. One pigmentary use is in coatings to impart a rough, nonslip surface. Bentonite [1302-78-9] is a colloidal clay which is incorporated in water and emulsion paints. Asbestos, ie, fibrous magnesium silicate, functions as a viscosity control agent. Glass spheres are inert fillers used in paints and plastics. In traffic paints, glass spheres are used for their reflective properties. They can be surface-coated with silane coupling agents and used in engineering-resin and thermoset systems. Calcium sulfate [7778-18-9], CaSO, is produced by calcining raw gypsum-$CaSO_4.2H_2O$. Calcium sulfate has a refractive index of 1.59, displays good heat resistance, and is used in composite pigments and as a filler in plastics and in primer-paint systems. A drawback of $CaSO_4$ is its solubility in water and sensitivity to the presence of moisture.

Barium carbonate [513-77-9] can be obtained naturally from the mineral witherite or it can be synthesized. Its uses are similar to those of barium sulfate. Sodium silico aluminate [1344-00-9] is an ultrafine synthetic pigment with a surface area of 130 m^2/g and an average particle size of 0.022 μm. It is used as a filler in paper and to extend TiO_2 in paints. Nepheline syenite [68187-64-4] is a naturally occurring sodium potassium aluminum silicate and is used primarily in the glass and ceramic industries.

Colored Pigments

Iron Oxides. In general, all iron oxides are characterized by low chroma and excellent lightfastness, and they are nontoxic, nonbleeding, low in cost, and independent of petroleum sources. However, properties vary for each iron oxide. For example, the reds provide good heat resistance, whereas the hydrated yellows undergo dehydration at 177°C. Zinc and magnesium ferrites are inert and heat-stable yellows are good for coating and plastic applications. The synthetic iron oxides are good replacements for the natural pigments because of a more uniform particle composition, greater purity, and higher tint strength.

Good dispersibility is achieved through jet milling and micronizing both natural and synthetic pigments. Efficient production procedures currently make use of computers and color-measurement techniques (38).

Sales of iron oxide pigments, including imports, amounted to 9.45×10^7 in 1977 (39). Domestic pigments are supplied by 19 companies. The largest single iron oxide facility in the United States is the 41,000-t/yr plant owned by Mobay Chemical and located at New Martinsville, West Virginia (see also Amines by reduction). The quantities and values of iron oxide pigment sales in the United States during 1977 are listed in Table 10.

Natural. Iron oxides are the most used of the colored pigments and are derived from natural and synthetic sources. The earth's crust contains 7 wt % iron oxides. Natural iron oxides are processed from several different ores including hematite [1317-61-9], limonite [1317-63-1], siderite [14476-16-5], and magnetite [1309-38-2] and provide a range of reds, yellows, purples, browns, and blacks. Although iron oxides are abundant, there are few deposits on the earth that contain acceptable colorant material. Persian Gulf red oxide comes from the hematite deposits on Ormuz Island in the Persian Gulf. Typically it contains 72 wt % Fe_2O_3, is associated with silica, and is considered the highest chroma red oxide of natural origin. Hematite deposits near Malaga, Spain, yield a less red iron oxide, commonly called Spanish oxide, which assays ca 85 wt % Fe_2O_3. Red oxides can be produced by calcination of limonites, hydrated iron oxides, siderite, and pyrite. Calcined pyrite cinders, a by-product in the manufacture of sulfuric acid, can be ground and air classified to obtain a red pigment. Persian Gulf reds have densities of 4.10–4.50 g/cm^3 with oil-absorption values of 11–22 kg/100 kg, whereas Spanish reds have densities of 4.17–4.46 g/cm^3 and oil absorption values of 10–16 kg/100 kg.

Some yellow iron oxides are mined in Georgia, Virginia, and Italy and are commonly known as siennas. The iron oxide content normally is 50–60 wt %. Silica and alumina are associated with these ores. Raw sienna is a dark yellow and is converted by calcination to burnt sienna which is a deep brown; both are somewhat transparent. The density and oil-absorption value of a typical raw sienna iron oxide is 3.44 g/cm^3,

Table 10. Finished Iron Oxide Pigments Sold in the United States in 1977[a]

Pigment	Quantity, t	Value, 10^3
natural		
black, magnetite	5,284	475
brown, iron oxide[b]	7,920	2,665
umbers		
burnt	4,517	2,480
raw	1,874	954
red		
iron oxide[c]	33,942	3,113
sienna, burnt	670	475
yellow		
ocher[d]	5,841	619
sienna, raw	642	361
Total	*60,690*	*11,142[e]*
synthetic		
brown iron oxide[f]	9,207	8,650
red iron oxides	23,875	23,884
yellow iron oxide	23,132	21,028
Total	*56,214*	*53,562*
other		
Total[g]	*10,745*	*9,147*
Grand Total	*127,649*	*73,851[e]*

[a] Ref. 40.
[b] Includes Van Dyke brown.
[c] Includes pyrite cinder.
[d] Includes yellow iron oxide.
[e] Data do not add to total shown because of independent rounding.
[f] Includes synthetic black iron oxide.
[g] Unspecified; includes natural and synthetic iron oxides.

and 28.6 g/100 g, respectively, as compared to 3.95 g/cm^3 and 32.9 g/100 g for a typical burnt sienna. Burnt sienna displays a hiding power of 72 m^2/kg (350 ft^2/lb) compared to 41 m^2/kg (200 ft^2/lb) for raw sienna.

Ochers are yellow iron oxides, are lighter in color than siennas and, in some cases, contain less Fe_2O_3 than the siennas. Sources for ochers include South Africa, India, France, and Georgia and Virginia in the United States. The highest quality ocher occurs in France and is contained in a limonite ore of 20 wt % Fe_2O_3. The U.S. deposits assay 50–60 wt % Fe_2O_3. Densities of natural ochers are 2.7–3.7 g/cm^3 and oil absorptions are 19–41 g/100 g. There are fewer grades of ochers sold in comparison to the siennas and other natural iron oxides.

Cyprus is the principal source of fine raw umber, which commonly is called Turkey umber. Raw umber has a deep greenish brown masstone. The ore contains ca 50 wt % ferric oxide which is associated with manganese dioxide, carbon, silicates, and combined water. Its distinctive deep color results from the combined effects of the iron oxide, carbon, and manganese dioxide. Burnt umber is produced by calcining raw umber; the hydrated water is lost with consequent conversion of the yellow iron oxide to red iron oxide and oxidation of much of the carbon. A typical natural umber has a density of 3.27 g/cm^3, a surface area of 102 m^2/g, a hiding power of 51 m^2/kg (250 ft^2/lb), and an oil absorption of 44 g/100 g. A typical burnt umber has a density of 3.69

g/cm^3, a surface area of 87 m^2/g, a hiding power of 51 m^2/kg (250 ft^2/lb), and an oil absorption of 56 g/100 g.

Other natural brown iron oxide pigments are derived from calcination of ores, eg, limonite and siderite. The darker or browner pigments are known as metallic browns and contain up to 98 wt % iron. Typical densities and oil absorptions are 4.0–4.9 g/cm^3 and 12–29 g/100 g, respectively.

Micaceous iron oxide is comprised substantially of Fe_2O_3 but it is gray. Its name is derived from its flakelike crystalline structure which resembles that of mica. The largest and best deposits are located in Austria but there also are deposits in the United Kingdom. The principal use of this pigment is in metal-protective coatings. The particles laminate in the film and form a highly reflective surface which reduces radiation degradation of the paint film, and the flaky structure provides a barrier to the penetration of moisture and fumes. Use of micaceous iron oxide is small in the United States.

Black natural iron oxide is manufactured from magnetite, and it is mined in a number of countries including Canada, South Africa, the USSR, and the United States. The iron content is ca 85–95 wt % Fe_3O_4 with the remainder comprised of silica and alumina.

Synthetic.   Synthetic iron oxides are red, yellow, brown, and black. Pigment properties are varied for the iron oxide reds. Densities are 4.5–5.2 g/cm^3, with the lower and higher densities being characteristic of the ferrite reds and calcined copperas, respectively. The variance in oil absorptions of 17–75 g/100 g results in part from the variety of particle shapes associated with these iron oxides; ie, spheroidal calcined copperas, acicular ferrite reds, rhombohedral and spheroidal precipitated reds, and cubical black. Hiding power for the group is 120–200 m^2/kg (600–1000 ft^2/lb).

Advantages of synthetic iron oxides over their natural counterparts include chemical purity, more uniform particle size and size distribution, and as in the case of precipitated types, the ability to be prepared in predispersed vehicle systems by flushing techniques. Manufacture of synthetic iron oxides involves three principal methods: precipitation of a soluble iron salt with an alkali and oxidation, organic reduction processes utilizing iron and calcination, and thermal decomposition of iron compounds and salts.

The principally used iron salt in the manufacture of iron oxide pigments is ferrous sulfate heptahydrate, $FeSO_4.7H_2O$ [7720-78-7], or copperas. Copperas is a by-product of the sulfate process involved in the manufacture of titanium dioxide pigment. It also is a by-product from steel mills, ie, in the spent pickle liquors, and can be produced by reaction of sulfuric acid with scrap iron. Other iron salts that serve as raw materials are ferric sulfate, ferrous chloride, and ferric chloride. Other materials for iron oxide pigment manufacture are scrap iron, eg, unalloyed stampings and punchings, and alkalies, eg, sodium hydroxide and ammonia.
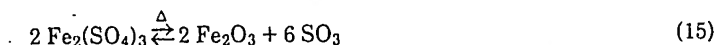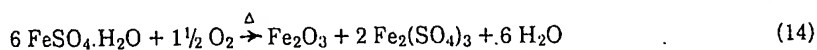
Preparation of copperas red involves calcination of ferrous sulfate by a two-stage process, the first involving the dehydration of the ferrous sulfate:

$$FeSO_4.7H_2O \xrightarrow{\Delta} FeSO_4.H_2O + 6\,H_2O \qquad (11)$$
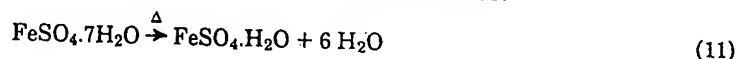
The second stage involves decomposition above 650°C in the absence of air:

$$6\,FeSO_4.H_2O \xrightarrow{\Delta} 2\,Fe_2O_3 + Fe_2(SO_4)_3 + 6\,H_2O + 3\,SO_2 \qquad (12)$$

$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3\,SO_3 \qquad (13)$$

or in the presence of air:

$$6\ FeSO_4.H_2O + 1\frac{1}{2}\ O_2 \xrightarrow{\Delta} Fe_2O_3 + 2\ Fe_2(SO_4)_3 + 6\ H_2O \qquad (14)$$

$$2\ Fe_2(SO_4)_3 \xrightarrow{\Delta} 2\ Fe_2O_3 + 6\ SO_3 \qquad (15)$$
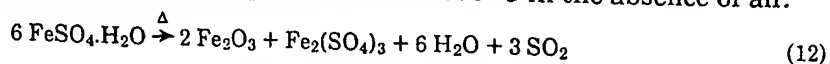
By-products of these reactions are reclaimed and recycled. The color depends on the size of the particle which forms, and the size is controlled by regulation of furnace-retention time and calcination temperature. The calcined product is ground, washed, and classified.

Preparation of ferrite red involves calcining synthetic yellow iron oxide and the process parallels the production of red from natural yellow oxides. Various yellows can be produced and, when dehydrated, provide reds that differ depending mainly on particle size; the finer the size, the lighter the shade. Calcination affects oil absorption by changing the structure of the particles, ie, the sintering causes rounding of the edges and pitting of the surfaces.

Direct precipitation of red iron oxides involve growth of iron oxide particles on specially prepared nucleating particles or seeds of Fe_2O_3. The precipitation conditions are critical because normal precipitation conditions tend to produce $Fe_2O_3.H_2O$. The particles are either spherical or rhombohedral, depending on the nucleating material.

Black iron oxide, Fe_3O_4 or $FeO.Fe_2O_3$, can be calcined at 370°C resulting in oxidation of FeO. The original cubic shape of the black iron oxide is retained.

A Venetian red iron oxide is prepared by calcining a mixture of iron sulfate and lime. The final product typically contains 40 wt % Fe_2O_3, 60 wt % $CaSO_4$.

Synthetic red iron oxides are prepared in a variety of grades from light reds to dark reds and they are sold under a variety of names, eg, Indian red, Turkey red, and Venetian red. The color range of Venetian red is not as wide as that of the other types and is limited to light shades.

The Penniman-Zoph process is employed in the manufacture of yellow iron oxides and involves the preparation of a seed or nucleating particle by alkali precipitation of ferrous sulfate. The reaction is carried out at a low temperature and with an excess of ferrous ion; the hydroxide then is oxidized to a hydrated ferric oxide:

$$FeSO_4 + 2\ NaOH \rightarrow Fe(OH)_2 + Na_2SO_4 \qquad (16)$$

$$4\ Fe(OH)_2 + O_2 \xrightarrow[FeSO_4]{} \underset{seed}{2\ Fe_2O_3.H_2O} + 2\ H_2O \qquad (17)$$
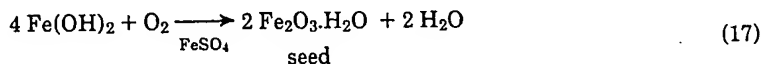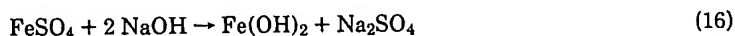
The seed is transferred to tanks containing scrap iron and ferrous sulfate solution and, while the seed is circulated over the scrap iron, air is bubbled through the medium causing the seed to grow as follows:

$$4\ FeSO_4 + 6\ H_2O + O_2 \rightarrow 2\ Fe_2O_3.H_2O + 4\ H_2SO_4 \qquad (18)$$
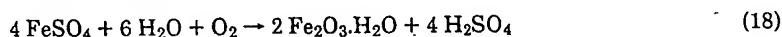
The ferrous iron is replenished by the action of the sulfuric acid on the scrap iron.

The complex reaction involves gas–liquid–solid interactions. Variables affecting production are temperature of reaction, circulation rate of oxygen, circulation rate of ferrous sulfate solution, and the size and shape of the seed particles which determine the shade of yellow. As the reaction continues over several days, larger particles, which are deeper and redder, develop. The reaction is stopped at the desired hue and the precipitate is washed free of soluble salts, dried carefully, ground, and bagged.

Brown and black synthetic iron oxides are made by sodium hydroxide precipitation of ferrous ion from a sulfate or chloride solution. The pigments form under alkaline conditions, with air oxidation, and at a boil. The pigments typically are cubic. In addition, browns often are prepared by blending red, yellow, and black synthetic iron oxides to the desired shade. The products of precipitation processes, ie, the yellows, blacks, and browns, can be calcined to reds and browns.

Magnetic gamma iron oxide, which is used in recording tape, is prepared from an acicular yellow iron oxide precursor (see Magnetic tape). The shape and size of the yellow iron oxide particles are controlled since they affect magnetic performance. Yellow α-iron oxide monohydrate [51274-00-1], α-Fe$_2$O$_3$.H$_2$O, first is dehydrated and then reduced with a reducing agent, eg, hydrogen, forming the black α-iron oxide [1309-37-1], α-Fe$_3$O$_4$, which is reoxidized to the brown γ-iron oxide [1309-37-1], γ-Fe$_2$O$_3$. Nitrobenzene reduction to aniline is achieved by means of iron filings or powder and other catalysts; iron oxides are produced as by-products (see Amines by reduction).

Zinc and magnesium ferrites are tan pigments and are formed from the interaction of iron oxides with metallic oxides:

$$\text{ZnO} + \text{Fe}_2\text{O}_3 \xrightarrow{\Delta} \text{Zn.Fe}_2\text{O}_4$$

(19)

Magnesium oxide can be substituted for the zinc oxide. The ferrites are more heat stable than the conventional hydrated yellow iron oxides. Typical properties of some synthetic iron oxides are compared in Table 11.

The principal use of transparent iron oxides is in metallic automotive finishes. Chemically they are the same as their opaque counterparts. Particle size differences between an opaque yellow iron oxide, a low opacity type, and a transparent type are illustrated in Figures 4a, **b**, and **c**, respectively.

The popularity of browns, yellows, and earth-tone colors and the demand trend away from heavy-metal, toxic pigments has helped increase sales of iron oxides. The largest use for iron oxides is in coatings and represents 50% of the synthetic pigments produced. Other areas of application include plastics, paper, ceramics, cement, roofing granules, and magnetic recording tapes.

Lead Chromates and Molybdate Oranges. Lead chromates and molybdate oranges provide a gamut of hues ranging from a greenish yellow through orange to light red. When blended with other pigments, mixtures of iron blue or phthalocyanine blue with chrome yellow produce green hues and blends of molybdate orange and organic pigments, eg, rubines or quinacridones, produce reds and maroons. The various hues of the lead chrome yellows, chrome oranges, and molybdate oranges depend on the interrelationship of three factors: chemical composition, crystal structure, and particle size. Four chemical types characterize this group of pigments.

Table 11. Typical Properties of Some Synthetic Iron Oxides

Property	Yellow	Brown	Black	Zinc ferrite
density, g/cm^3	4.05	4.70–4.95	4.95–5.18	5.24
oil absorption, g/100 g	50–60	24	18–28	44–49
refractive index	2.3–2.4	3.0	2.42	2.5
hiding power, m^2/kg[a]	72	180–200	180–250	80

[a] To convert m^2/kg to ft^2/lb, divide by 0.2048.
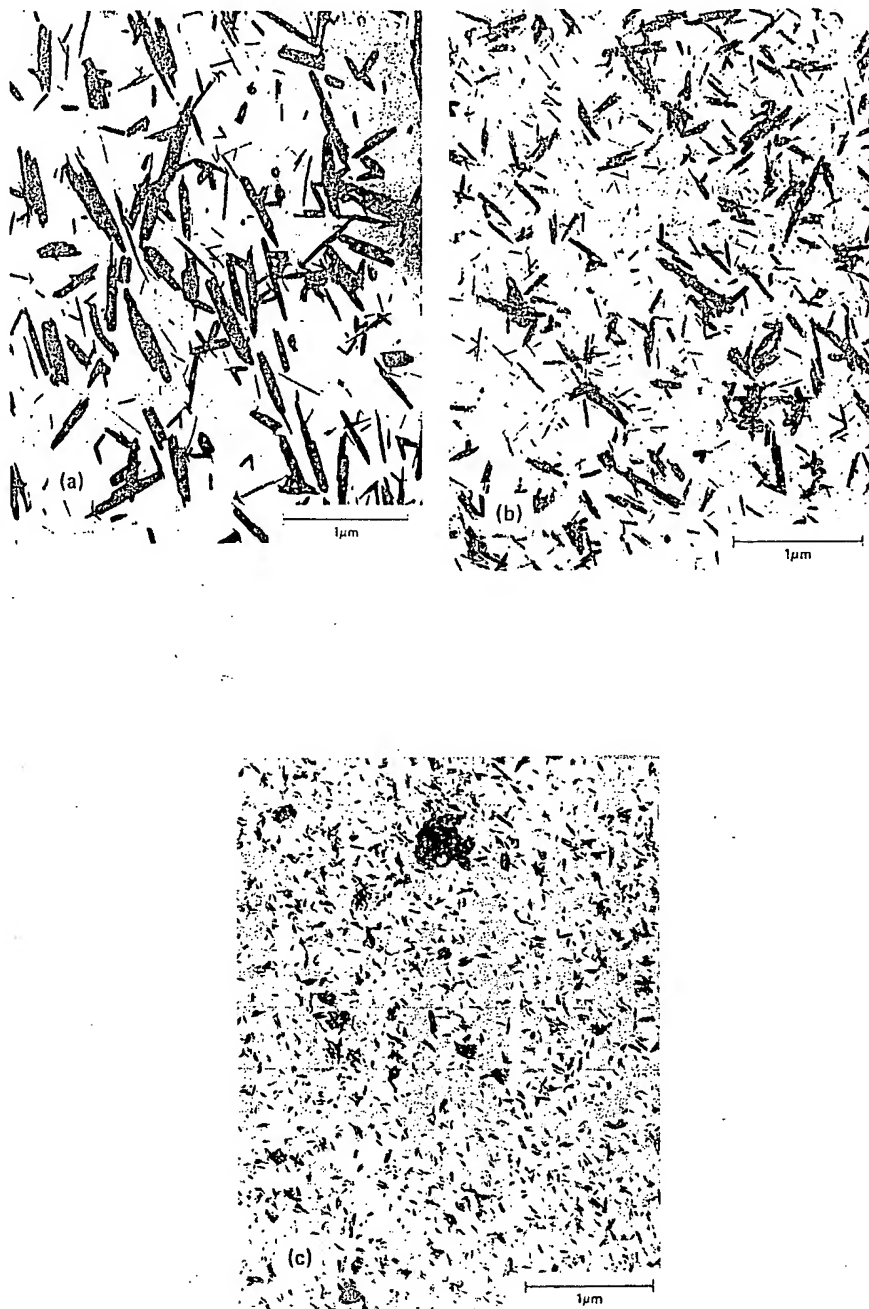
Figure 4. Electron photomicrographs of yellow iron oxide with different particle sizes. (a) Opaque type. (b) Low opacity type. (c) Transparent type.

Medium chrome yellows are essentially pure $PbCrO_4$ and provide the reddest yellow hue. Primrose chrome yellow and light chrome yellows are solid solutions of lead chromate and lead sulfate, and the ratios of the two components can be varied to control the shade. At nearly similar chemical composition, the primrose and light chrome yellow are noticeably different in hue because of the polymorphic nature of lead chromates which allows precipitation of two different crystal structures. Primrose chrome yellow is characterized by the unstable orthorhombic crystal structure and light chrome yellow is monoclinic. Stabilizers are added to the primrose variety during processing to prevent hue shifts and detrimental conversions.

Chrome oranges are $PbCrO_4 \cdot PbO$ and the variation of hue from light to dark orange is more a consequence of change in particle size, with the dark shades associated with large particles. Chrome orange is characterized by a monoclinic unit cell.

The fourth chemical type is molybdate orange. These pigments represent solid solutions of lead chromate, lead molybdate, and lead sulfate and display hues from orange to light red. Various phases of the $PbCrO_4$–$PbMoO_4$ system have been reported (41). A 90 wt % $PbCrO_4$–10 wt % $PbMoO_4$ phase is comprised of monoclinic cells which are slightly distorted from tetragonal cell structure. The composition of commercial products excluding after treatments is 75–90 wt % lead chromate. The chemical compositions of lead chromates are listed in Table 12 (42).

Lead chromates are prepared by precipitation techniques from soluble salts in aqueous media. Precipitation is followed by chemical treatment where applicable, filtration or pressing, washing, drying, and grinding. The raw material list includes a number of different lead compounds, eg, litharge, lead nitrate, basic lead acetate, basic lead carbonate, as well as acids, alkalies, sodium bichromate, and sodium chromate.

Reaction of lead nitrate with sodium bichromate causes precipitation of the highly insoluble $PbCrO_4$:

$$2\,Pb(NO_3)_2 + Na_2Cr_2O_7 + H_2O \rightarrow 2\,PbCrO_4 + 2\,NaNO_3 + 2\,HNO_3 \qquad (20)$$
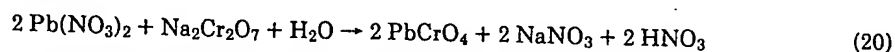
Production of HNO_3 lowers the pH of the pigment slurry and, thus, increases the solubility of the lead chromate. This redissolving effect causes growth of the larger pigment particles; improper control of the growth leads to poor pigmentary characteristics. Control of particle growth is either by introduction of lead carbonate or an equivalent which allows regeneration of lead nitrate or by changing the lead source from lead nitrate to basic lead acetate. Because acetate chrome yellows tend to darken more on exposure than nitrate-based chromates, the former need to be washed more thoroughly.

Manufacture of primrose and light chrome yellows requires coprecipitation of lead chromate and lead sulfate. Precipitation conditions are controlled to effect proper crystal structure formation. The light chrome yellows are precipitated hot and with excess lead, whereas the primrose hue is precipitated at lower temperatures.

Chrome oranges are precipitated under alkaline conditions. The particle size, which affects the hue, is controlled by the degree of alkalinity. The more alkaline condition results in large particles, deep hue, and weak tints. Chrome oranges are not surface-treated.

Molybdate oranges were prepared, patented, and marketed in the 1930s (44). Molybdate orange is prepared by the addition of Na_2CrO_4, Na_2MoO_4, and Na_2SO_4 to $Pb(NO_3)_2$. Under proper conditions $PbCrO_4$, $PbMoO_4$, and a small amount of $PbSO_4$

Table 12. Chemical Composition and Typical Properties of Lead Chromates[a,b]

Pigment type	Chemical composition, wt %				Density, g/cm^3	Oil absorption, g/100 g
	PbCrO$_4$	PbSO$_4$	PbO	PbMoO$_4$		
primrose chrome yellow	52.0–82.7	4.2–25.9			5.51–5.73	45.9–47.7
light (lemon) chrome yellow	52.4–68.8	17.4–39.0			5.44–6.09	45.3–50.7
medium yellow	82.4–98.2				5.58–6.04	46.6–50.3
chrome orange (light and dark)	58.2		39.2–39.6		6.62–7.07	55.1–58.8
molybdate orange	66.3–80.0	2.3–8.8		9.2–15.1	5.41–6.34	45.0–52.8

[a] Refs. 42–43.
[b] Based on analysis of commercial pigments manufactured by CIBA-GEIGY Corporation, Pigments Department, Glens Falls, N.Y.; variations in composition exist when compared to other pigment manufacturers' products. Analysis not adjusted for chemical end treatments where applied.

coprecipitate as a solid solution. The reaction is complex, because of the three lead compounds involved, lead molybdate, lead chromate, and lead sulfate; the latter two are polymorphic. Formation of lead chromate, an undesirable side reaction, is minimized during manufacture because it leads to the formation of dull and weaker colors. Because molybdate oranges are characterized by an unstable crystal habit, proper stabilization to prevent conversion is carried out after precipitation. Chemical composition ranges for molybdate oranges are listed in Table 12.

Most lead chromates are surface-treated with various inorganic and/or organic compounds. End-treatments enhance the working and performance properties of the pigment, eg, wetting, texture, heat stability, and lightfastness and they aid in the control of crystal growth and prevent conversion of a metastable form. Compounds used for these purposes include hydrous oxides; silicates and phosphates of elements, eg, aluminum, titanium, and zirconium; rare earths; tin or antimony compounds; and organics, eg, fatty acids (45–46). Deficiencies, eg, poor sulfide and chemical resistance and poor heat stability, are remedied by encapsulating lead chromate and molybdate orange pigments with silica, which provides an efficient and impervious coating (see Microencapsulation) (47). Figure 5 shows a lead chromate that has been coated with a large amount of amorphous silica. Pigments that are resistant to atmospheres high in SO_2 also are marketed, particularly in Europe.

Of the yellow lead chromates, chrome oranges, and molybdate oranges, hiding power is greatest with the molybdate oranges which achieve values 1.5 times greater than medium chrome yellow and values 2 to 3 times greater than light and primrose chrome yellows. Refractive indexes for monoclinic $PbCrO_4$, rhombic $PbCrO_4$–$PbSO_4$, and chrome orange are 2.3–2.66, 2.11–2.4, and 2.4–2.7, respectively (48). Particle sizes are 0.1–1.0 μm. Chrome oranges are larger, a maximum size of ca 12 μm. These pigments are nonbleeding in various organic solvents as well as in water. Alkali and acid resistance is fair to poor. Lead chromate pigments darken on exposure, both in masstone and tint applications. Predarkened and other improved lightfast products are marketed. The mechanisms involved in discoloration of these pigments have been described (49).

Chrome yellows and molybdate oranges are soft textured. Generally, their dispersibility results in proper pigment grind development and high gloss suitable for topcoat finishes. Because dark chrome oranges and some very red molybdate oranges

0.1 μm

Figure 5.   Electron photomicrograph of a silica-encapsulated lead chrome yellow.

are comprised of large particles, they are sensitive to grinding. Overgrinding causes hue shifts as the ultimate particles are fractured and reduced in size. Overgrinding also removes chemical end-treatments, ie, silica. Lead chromates and molybdate oranges display good bake resistance. They tend to react with highly acid vehicles.

A comparison of chrome pigment shipments from 1972 to 1977 indicates an increase of 450 metric tons in chrome yellow and orange use to 2.95×10^4 t in 1977 (22). The value of these shipments nearly doubled from 2.45×10^7 in 1972 to 4.95×10^7 in 1977. Consumption of chrome oranges has decreased because better pigment performance can be obtained from blends of molybdate orange and medium chrome yellow. Shipments of molybdate orange have increased 7.3% from 1.12×10^4 t in 1972 to 1.20×10^4 t in 1977.

Chrome yellows, oranges, and molybdate oranges are used in a large number of different paint systems, which are restricted mostly to maintenance and industrial finishes because of their toxicity and potential carcinogenic nature. Medium yellow shades are used in traffic-paint formulations. Blends of molybdate oranges with organic reds and violets produce low cost, durable automotive finishes. Molybdate oranges and chrome yellow, especially the primrose type, are two of a few colored inorganic pigments used by the printing industry. Plastic applications are limited for the regular type lead chromate pigments. Heat-resistant types, eg, Krolor (DuPont) and Rampart HR (CIBA-GEIGY), are suitable as colorants in a wider range of plastic materials than regular types.

Normal Lead Silicochromate. Normal lead silicochromate is manufactured by coating a core of silica with a medium yellow lead chromate. The composition is 50 wt % $PbCrO_4$–50 wt % SiO_2. The pigment was introduced in 1963, primarily for use in traffic paints. The greater thickness of the applied paint film reduces the hiding power factor between this pigment and a corresponding regular lead chromate medium yellow.

Cadmiums. Cadmium pigments provide a range of brilliant colored pigments from the greenish, primrose yellow through orange, red, and maroon. This hue range is based on the pigment manufacturer's ability to vary the chemical composition from pure cadmium sulfide, which is golden yellow, to other hues by preparation of solid solutions or mixed crystals of cadmium sulfide with other metal sulfides or cadmium selenide. The cadmium yellows are solid solutions of varying percentages of cadmium sulfide and zinc sulfide, and cadmium oranges, reds, and maroons are solid solutions of varying composition of cadmium sulfide and cadmium selenide.

The increasing use of selenium metal by the electronics industry caused an acute shortage of this metal for pigment production during the late 1940s and early 1950s but led to the development and introduction in 1955 of the Mercadium pigments (50). These pigments are based on cadmium sulfide–mercury sulfide solid solutions, and variation in chemical composition yields a hue range somewhat parallel to the selenide oranges, reds, and maroons. Chemical compositions necessary to produce the various characteristic hues are listed in Table 13.

At 25°C, a typical golden cadmium yellow concentrate has a specific gravity of 4.78 and an oil absorption of 19 g/100 g. The corresponding golden yellow lithopone, which contains 60 wt % barium sulfate, has a specific gravity of 4.55 and an oil absorption of 17 g/100 g. Cadmium selenide oranges have similar values for oil absorption. A deep orange concentrate is characterized by a specific gravity of 5.07 compared to 4.54 of the lithopone. A typical medium light red concentrate has a specific gravity

Table 13.   Typical Chemical Compositions and Related Hues for Cadmium Pigments[a]

	Compositions, wt %			
	CdS	ZnS	CdSe	HgS
cadmium yellow, concentrated				
primrose	79.5	20.5		
lemon	90.9	9.1		
golden	93.4	6.6		
deep golden	98.1	1.9		
cadmium sulfoselenide orange-reds, concentrated				
light orange	85.0		15.0	
light red	67.5		32.5	
medium light red	58.8		41.2	
medium red	51.5		48.5	
dark red	44.8		55.2	
maroon	35.0		65.0	
Mercadium orange-reds				
deep orange	89.0			10.9
light red	83.4			16.6
medium light red	81.0			19.0
medium red	78.5			21.5
dark red	71.6			23.9
maroon	73.5			26.5

[a] Cadmium pigments manufactured by CIBA-GEIGY.

of 5.22 and an oil absorption of 20 g/100 g. A medium light red lithopone, ie, containing 60 wt % barium sulfate, has a specific gravity of 4.58 and an oil absorption of 17 g/100 g. A Mercadium medium red concentrate has a specific gravity of 5.20 and an oil absorption of 19 g/100 g. Its corresponding lithopone has a specific gravity of 4.58 and an oil absorption of 18 g/100 g. Shipments of cadmium sulfide pigments in 1977 were 2300 t worth 9.8×10^6 (22).

Cadmium pigments are expensive and, where applicable, the lithopone forms are used. Lithopones are the concentrated pigments prepared with coprecipitated barium sulfate which acts as an extender. Lithopones contain ca 40 wt % concentrated pigment and ca 60 wt % barium sulfate.

Commercial preparation of a cadmium pigment is a two-step process, the first step of which is precipitation of the metal sulfide. The following chemical equations illustrate the preparation of a cadmium yellow.

$$CdSO_4 + Na_2S \rightarrow CdS + Na_2SO_4 \tag{21}$$

$$CdSO_4 + BaS \rightarrow CdS + BaSO_4 \tag{22}$$
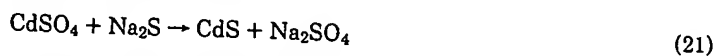
Equation 21 illustrates the formation of a concentrated pigment and equation 22 illustrates the formation of a lithopone. Use of Na_2S allows the formation of Na_2SO_4 which is removed by washing. Substitution of BaS for Na_2S results in direct coprecipitation of the extender for a lithopone. The in situ formation of $BaSO_4$ yields a superior, higher quality pigment than that produced from a mechanical mixture of barium sulfate and concentrated pigment.

Following the controlled precipitation and washing of the pigment, it is necessary to develop the color and pigmentary properties by calcination or heat treatment. The

hexagonal crystal habit of cadmium sulfide is achieved by controlled heating above 400°C, usually at 600–700°C, in an inert or reducing atmosphere. Calcination time and temperature affect particle size; the longer the calcination or the higher the temperature, the larger the pigment particle which, in turn, results in lower tinting strength and darker hues. Commercially available cadmium pigments are based on the hexagonal crystal structure. Introduction of ZnS for the lighter yellows or CdSe or HgS for the formation of oranges and reds results in only slight distortions of the crystal lattice (51). Cadmium pigment particles are ca 0.2–0.8 μm in diameter.

Cadmium pigments display clean, bright hues; heat stability up to and, in some cases above 400°C; excellent bleed and alkali resistance; fair acid resistance; and good tint lightfastness when protected from moisture. The heat stability of cadmium makes these pigments chief colorants for plastics, ceramic glazes, and enamels. The exceptions are the Mercadiums which are not as heat-stable as their sulfoselenide counterparts and cannot be recommended for processes in which heats of 400°C or greater are developed. Concentrated pigments are more heat-stable than the lithopones.

Cadmium colorants are used in artists' paints, heat-resistant coatings, printing inks, latex paints, rubber goods, leather goods, and coated fabrics. Exterior use of cadmium pigments is problematic because of their sensitivity not to light alone, but to a combination of light and moisture. This drawback can be remedied partially by prudent formulation with selected types of cadmium pigments and use of less moisture-sensitive vehicles, film formers, and extender pigments for tints.

Synthetic Mixed Metal Oxides. Synthetic mixed metal–oxide pigments are unlike the precipitated inorganic pigments in that they are products of solid-state chemical reactions at high temperatures. Traditionally they are used by the ceramic and glass industries, but some have become popular for use in coatings and plastics. Egyptian blue, a colorant prepared from a mixture of calcium and copper silicate, was used in antiquity. Smalt, a potassium glass doped with cobalt oxide, was prepared during the mid-1500s. Cobalt blue was synthesized in 1777. Colored rutile titanium pigments were patented by DuPont in the early 1940s (52).

Manufacturing steps include selection and proper mixing of raw materials which are blended according to dry or wet mixing techniques. Soluble components precipitate upon introduction of appropriate alkalies. Mixing provides for the intimate contact of the raw materials which are placed either in an open or closed sagger. They then are calcined in a tunnel kiln or other type of furnace at 550–1400°C. The high kiln heat provides the necessary energy for reaction and provides for stabilization of the resultant compound for later application.

Synthetic mixed metal oxide pigments can be classified several ways, one of which is by crystal structure. Two important types are mixed-phase rutile pigments and mixed-phase spinel pigments. Examples of these pigments and their colors, chemical compositions, and crystal structures are listed in Table 14.

Rutile titanium dioxide acts as a host lattice for the yellow colorant formed from antimony and nickel oxides at 980°C. Chrome antimony buff is another rutile type; under high heat, ions of chemical compounds are added as dopants and diffuse into the host matrix. Cobalt blue forms from the reaction between cobalt oxide and alumina at >1000°C. Partial substitution of chromium for the aluminum and variation of their ratio can alter the color from blue to blue-green.

These various colorants show excellent stability to heat. They display excellent weather resistance and lightfastness, are nonbleeding and nonmigrating, and are

Table 14.   Formulas, CAS Registry Nos., Colors, and Crystal-Habit Characteristics of Some Mixed-Phase Synthetic Oxide Pigments for Coatings and/or Plastics

Name[a]	CAS Registry Number	Chemical composition or formula[b]	Crystal structure
nickel antimony titanium yellow	[8007-18-9]	$(Ti,Ni,Sb)O_2$	rutile
chrome antimony titanium buff	[68186-90-3]	$(Ti,Cr,Sb)O_2$	rutile
cobalt chromite green	[68187-49-5]	$CoCr_2O_4$	spinel
cobalt aluminate blue	[1333-88-6]	$CoAl_2O_4$	spinel
cobalt titanate green	[68186-85-6]	Co_2TiO_4	inverse spinel
iron titanate brown	[68187-02-0]	Fe_2TiO_4	inverse spinel
copper chromite black	[12018-10-9]	$Cu(CrO_2)_2$	spinel

[a] Ref. 53. Dry Color Manufacturer's Association classification and chemical description of mixed metal–oxide inorganic colored pigments as defined by Metal Oxides and Ceramic Colors Subcommittee in 1978.
[b] Composition may be modified with addition of other components.

chemical-resistant, especially to acid and alkalies. As a group, their main weakness is lack of color intensity both in masstone and tint when compared to conventional pigments. Attempts to prepare rutile types with smaller particles results in poorer color intensity. Another disadvantage is higher cost.

Nickel antimony titanium yellow and chrome antimony titanium buff are not stable above 1000°C. Thus, they cannot be used in glazes, but they are used in vitreous enamel and plastics. Nickel antimony titanium yellow is incorporated in house-paint formulations, automotive finishes, and coatings for metal and plastic sidings. In siding applications, it chalks in the pigment color. Nickel antimony titanium yellow has a specific gravity of 4.3, an oil absorption of 13 g/100 g, and an average particle size of 1 µm.

Cobalt blue is used primarily as a colorant for the ceramics industry but also is applied in coatings and plastics. Its density and oil absorption are 4.2–4.3 g/cm^3 and 27–36 g/100 g, respectively.

Iron Blue.   Iron blue or Prussian blue, when first developed in Berlin in 1704, was a hard-textured, difficult-to-grind pigment. However, an iron blue that was easier to grind and disperse was developed by A. Milori Co. in France. Modern iron blues are ferric ammonium ferrocyanides. They are as good or better than the pre-World War I potassium types and were developed in the United States as a consequence of a shortage of potassium during that period.

Common iron blues are Milori, Chinese, Prussian, and Toning blues. Chinese blues are characterized by jet masstones and develop greenish-blue tints. Prussian blues also have jet masstones but are redder and are less intense in tint than Chinese blue. The jet masstone of the Chinese and Prussian blues enables their use in shading of blacks. Milori blues are reddest in masstone. The properties of a Chinese blue and a Milori blue are compared in Table 15. Toning blues possess the reddest tints and the redness is fugitive. Use of toning blue to increase the jetness of black inks has diminished because of the increased use of alkali blue, an organic pigment.

Some soluble blues are water-dispersible colloidal blues and are used for coloring paper, for bluing, and in other applications. Iron blues are used in printing inks, except glycol types, many kinds of paint systems and enamels, carbon paper, certain plastics, eg, low density polyethylene, and are blended with chrome yellow to produce greens. Iron blues act as catalysts in rubber and vinyls, and degrade the products when exposed

Table 15. Comparison of Properties of Two Iron Blues (Chinese and Milori)

Property	Milori blue	Chinese blue
masstone	plum; less jet	mostly jet
tint color	reddish blue	greenish blue
tint strength[a]	weak	strong
oil absorption[a]	low	high
dispersibility[a]	easy	hard
particle size[a]	large	small

[a] Values are relative only with regard to Milori blue and Chinese blue.

to heat or uv radiation. The poor alkali resistance of iron blues is a prominent drawback; however, alkali resistance has been improved by treating the pigment with nickel compounds. Iron blues are not recommended for use in water-based inks and paints that have alkaline pHs. Densities and oil absorptions of iron blues are 1.7–1.85 g/cm^3 and 33–56 g/100 g, respectively.

Preparation of iron blue is based on the oxidation of Berlin white [1344-36-1], $Fe(NH_4)_2[Fe(CN)_6]$, which is produced by reaction of sodium ferrocyanide, ferrous sulfate, and ammonium sulfate. The Berlin white is digested hot with sulfuric acid and, following digestion, is oxidized with sodium chlorate or sodium bichromate to $Fe(NH_4)[Fe(CN)_6]$. After oxidation, the iron blue is filtered, washed, dried, and packaged. Iron blues contain residual moisture, often up to 8 wt %, and tend to absorb moisture under humid conditions and release moisture when the atmosphere is dry. High moisture facilitates aggregate size reduction. At deep shades, iron blues are characterized by good lightfastness but tend to bronze. Bronzing is the development or exposure of a reddish surface. Iron blues are reduced in the presence of oxidizable vehicles and tend to lose their color on storage. This corrects itself somewhat when the paint is brushed out and exposed to air which causes reoxidation of the blue.

Ultramarines. Lapis lazuli (lazurite) was the natural source of ultramarine blue for hundreds of years. The first German patent issued in 1877 was for the manufacture of ultramarine red (54). The composition of ultramarine blue varies within certain ranges: Na_2O, 19–23 wt %; Al_2O_3, 23–29 wt %; SiO_2, 37–50 wt %; S, 8–14 wt %. The position of the various elements within the cubic cell have been assigned (55). Typical ultramarine blues exhibit densities of 2.2–2.7 g/cm^3 and oil absorptions of 25–39 g/100 g, according to results from a modified ASTM 2281-31 method. The violets exhibit densities of 2.34–2.36 g/cm^3 and oil absorptions of 33–35 g/100 g.

Ultramarine blue provides good brilliance and, when used as a self-color in oil paints, it is transparent. It provides good resistance to heat, good lightfastness, and alkaline stability. Its applications include printing inks, textiles, rubber, artists' colors, plastics, cosmetics, and laundry blue. One drawback is its sensitivity to weak acids; this has been remedied to some extent by surface treatment with silica or silicic acid coatings. Ultramarine blue is no longer manufactured in the United States.

Today, ultramarine blue is prepared from intimate mixtures of china clay, sodium carbonate, sulfur, silica, sodium sulfate, and a carbonaceous reducing agent, eg, charcoal, pitch, or rosin. The blended and ground mixture is placed in saggers or crucibles which are heated in muffle furnaces. Over a 2–6-d period the mixture is heated to 785–800°C. The ingredients react to form a nonstoichiometric inorganic complex with a crystal structure similar to a zeolite (see Molecular sieves). The furnace
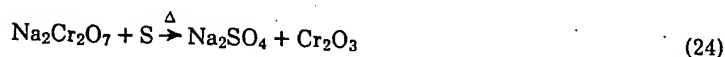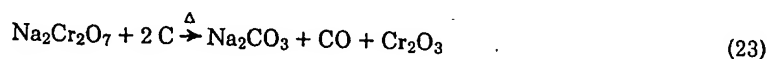
is cooled gradually for several days. The primary or crude ultramarine is processed by crushing, then is washed to remove soluble salts, classified into various particle-size grades by fractional sedimentation, and dried. The graduated particle-size fractions can then be blended into the desired products. Varying particle size and chemical composition controls the hue. Large particles, 3–5 μm in diameter, are characterized by dark masstones and become red upon tinting, whereas a lighter masstone is produced from 0.5–1.0-μm particles which produce stronger, greener tints (56).

In the production of violet and red ultramarines, blue ultramarine is treated with hydrogen chloride or with chlorine gas at 257°C or reacts with ammonium chloride. During the reaction, a color shift occurs resulting from rearrangement in the chemical composition of the molecule (57). The intensity of the red or violet depends on reactant concentrations, and time and temperature schedules during processing.

Manganese Violet and Cobalt Violet. Manganese violet and cobalt violet [10101-56-1], $CoNH_4PO_4.H_2O$, are prepared by precipitation techniques. They both display very good weathering and lightfastness and are nonmigrating. Manganese violet is characterized by a density of 2.82 g/cm³, an oil absorption of 25 g/100 g, and an average particle size of 1.5 μm. It is used in cosmetics and to tone white pigments. Typical properties of cobalt violet are density, 2.27 g/cm³; oil absorption, 20 g/100 g; and average particle size, 2.1 μm.

Chromium Oxide Green. Chromium oxide green is characterized by outstanding lightfastness with excellent resistance to acids, alkalies, and high temperatures. Because it weathers extremely well, chromium oxide green is applied as a colorant for roofing granules, cement, concrete, and outdoor industrial coatings. It also is used in ceramic applications. Chromium oxide green is a one-depth, drab olive green. A drawback in some applications is its abrasiveness.

Chromium oxide green is a calcined pigment and is prepared by reduction of sodium bichromate with sulfur and/or carbonaceous materials:

$$Na_2Cr_2O_7 + 2\,C \xrightarrow{\Delta} Na_2CO_3 + CO + Cr_2O_3 \tag{23}$$

$$Na_2Cr_2O_7 + S \xrightarrow{\Delta} Na_2SO_4 + Cr_2O_3 \tag{24}$$

The product is quenched, washed, dried, and ground.

One unique feature of chromium oxide green is that it reflects ir radiation and is similar in reflective properties to chlorophyll; therefore, it is used extensively in formulating camouflage coatings. Chromium oxides have specific gravities of 5.09–5.18 and oil absorptions of 12–23 g/100 g.

Hydrated Chromium Oxides. Hydrated chromium oxides are brilliant greens and are referred to as Gingnet's green. They exhibit a limited hue range, are semitransparent and of low opacity, but provide excellent lightfastness and alkali resistance. Water of hydration limits heat resistance of the pigment to application temperatures up to 260°C; thus, the pigment is unsuitable for ceramic use. Transparency permits formulation of polychromatic finishes. Its consumption has diminished since the introduction of phthalocyanine green in the 1940s.

Hydrated chromium oxide greens are manufactured by hydrolyzing a complex chromium borate obtained by heating sodium bichromate with boric acid in a furnace. A typical hydrated chromium oxide has a specific gravity of 3.40 and an oil absorption of 57 g/100 g.

Chrome Greens. Chrome greens represent blends of variable composition of mainly primrose chrome yellow and iron blue; they are available for use in their pure forms or they can be reduced with extender pigments. Available representative commercial blends contain 2 wt % blue for a light green and 65 wt % blue for a deep green. A redder primrose yellow is used in the blend to obtain a more olive shade green. Chrome green tints are important and their hue is bluish green. More bluish green tints result from the use of weaker, larger particle, chrome yellows. The density and oil absorption of a light chrome green are 4.9 g/cm^3 and 25 g/100 g, respectively. The same properties for a deep chrome green are 2.59 g/cm^3 and 35 g/100 g, respectively.

Chrome greens can be prepared by blending of the dry pigments, blending slurry or wet forms of the pigments, and precipitation of lead chromate in the presence of iron-blue slurry. A shading yellow or yellow for green pigment also is available.

Prior to World War II, chrome greens were the most popular greens. Their use has diminished because of the potential toxicity problem created by the use of lead chromate yellow in the blend and the advent of phthalocyanine green which has better performance properties. Chrome greens still are used in paints, printing inks, flooring materials, plastics, and paper goods because of their characteristic high chroma and excellent hiding power, ca 250 m^2/kg (1200 ft^2/lb). Drawbacks include susceptibility to darkening of the chrome yellow component in a sulfide atmosphere and the high pH which destroys the blue component. Blending chrome yellow with flocculation-resistant phthalocyanine blue results in better chemical resistance, improved package stability and improved lightfastness, particularly with tints.

Vermilions. Natural mercuric sulfide, HgS, can be derived from the mineral, cinnabar. As a pigment, HgS, is called vermilion and occurs in two forms, red crystalline or black amorphous. Vermilion in the red hexagonal crystal form can be prepared by addition of Hg to alkali sulfide followed by heat treatment. Vermilion is a tinctorially weak pigment, is sensitive to uv light, is moderately stable to heat, but has stability to alkali. Antimony vermilion [1317-86-8], Sb_2S_3, varies in hue from orange to red.

Van Dyke Brown. Van Dyke brown [52081-69-3] is a natural pigment. It consists principally of as high as 92 wt % organic matter, water and trace materials, eg, iron oxide, alumina, and alkali oxides. Most Van Dyke brown occurs in peat beds in the FRG. It is brownish black with a purplish-brown tint, and is used as an art pigment and in staining compounds. Its specific gravity is 1.5–1.66.

Black Pigments

Carbon Blacks. Carbon black is one of the oldest pigments in use. Carbon black is increasingly used as a pigment in nonrubber applications, eg, plastics, paints, and printing inks (58). For these applications, special carbon blacks have evolved to meet specific use requirements.

Approximately 90% of the carbon blacks produced are manufactured by the oil-furnace black process. The remainder are produced by other processes, eg, thermal, lamp black, channel, and acetylene processed. The reason for this variety of processes, is that there exists a unique link between manufacturing process and performance features of the carbon black and not all features are attainable by the furnace process (see Carbon).

The feedstocks for the oil-furnace process are essentially hydrocarbon oils. They

are specified to be free of coke and other gritty materials, possess high aromaticity, and contain low levels of asphalt, sulfur, and alkali metals. The oil-furnace process involves a partial combustion of the hydrocarbon feed, followed by quenching to reduce the temperatures rapidly from 1300–1600°C to 1000°C, which protects the newly formed carbon black aggregates. The product passes through heaters, where the combustion air is preheated, and is quenched again at 270°C prior to collection of the carbon black in glass bag filters. The carbon black is ground or micropulverized and stored. Carbon blacks are pelletized by dry or wet methods to provide a low dusting or nondusting product.

Thermal and acetylene blacks are prepared by hydrocarbon decomposition at high temperatures in the absence of air. The production of carbon blacks by the lamp black process is small. Other blacks based on carbon are graphite, bone black, vegetable blacks, and mineral blacks.

Selection of a carbon black depends on the black's performance characteristics, which are governed by particle size, surface area, structure or morphology, chemical composition, and surface chemistry. Carbon blacks are intermediate in crystallinity between the crystalline graphite and the amorphous structure of coal. Carbon blacks have surface areas of 6–1100 m²/g and particle sizes of 10–500 nm. With carbon black the term particle does not refer to an individual, discrete particle, but to a group of particles which are fused together and form a primary aggregate. The structure of carbon black is controlled during manufacture and is characterized as low, medium, or high; these designations refer to the size and configuration of the primary aggregates. High structure carbon blacks consist of relatively large, highly branched aggregates, whereas low structure blacks are composed of compact aggregates.

Typical properties of carbon black pigments as they relate to particle size and structure are listed in Table 16. Carbon blacks have a density of 1.8 g/cm³. Oil-absorption values differ. One method which is employed to measure oil absorption is the use of a Brabender/Cabot absorptometer by which the dibutyl phthalate (DBP) absorption number is determined. Some typical DBP absorption values are acetylene black, 250 mL/100 g solvent; thermal black, 33 mL/100 g; lamp black, 130 mL/100 g; furnace black, 103 mL/100 g and channel black, 100 mL/100 g.

Formulation of carbon black into coatings and printing inks changes the rheological properties of the system. At very low loadings of certain carbon–binder systems, Newtonian flow takes place. As loadings increase, the systems yield plastic or pseudoplastic flow and, at higher carbon loadings, the result is dilatant flow. Viscosity of carbon black pigmented vehicle systems predominantly is affected by the physical properties of the carbon black and less so by the chemistry of the surface. Certain

Table 16. Typical Properties of Carbon Black Pigments as Related to Particle Size and Structure

Property	Particle size		Structure	
	Large	Small	Low	High, ie, branched
masstone	grayer	darker		
tinting strength	weaker	stronger		
tinting undertone	bluer	browner		
oil absorption/viscosity	lower	higher	low	higher
dispersibility	easier	harder	harder	easier
loading capacity			higher	lower

carbon blacks are designated as long-, medium- or short-flow blacks. These designations define differences of flow characteristics in lithographic varnishes.

U.S. carbon black plant capacity in 1979 was 2.0×10^6 t but production amounted to ca 1.5×10^6 t with a commercial value of more than $\$6 \times 10^8$. The bulk of carbon black produced is consumed by the rubber industries, eg, by the tire industry as a reinforcing agent. Approximately 2% of the production was applied to plastics, ca 2.5% to printing inks, 0.5% to paint, and 3.0% to other nonrubber uses (59).

Graphite is a crystallized carbon that occurs in nature in different forms and it can be prepared synthetically. The density of graphite is ca 2.2 g/cm³. Oil absorption, blackness of color, and tinting strength are low. Because of its lubricating properties, it is used in lead pencils and stove polishes. It also is used in electrically conducting films.

Bone blacks are characterized by low oil absorption and low tinting strength relative to carbon blacks, but they do exhibit a very black color. Bone blacks are ca 20 wt % carbon with the remainder being calcium phosphate. They are used primarily for artist colors, tints, and artificial-leather coatings.

Vegetable blacks contain 50–94 wt % carbon; the remainder is mineral matter. Tint value and blackness are low. Occasionally they are used as fillers.

Mineral blacks are produced from materials, eg, coal and coke. They are low in color and tinctorial values, and are used principally as fillers.

Specialty Pigments

Zinc Yellow (Zinc Chromate). Zinc yellow, is a complex hydrated zinc potassium chromate (see Table 1). Its hue is greenish yellow, somewhat like a primrose lead chromate but it is weaker chromatically and lower in hiding power. Density and oil absorption values of zinc yellows are 3.36–3.49 g/cm³ and 28–31 kg/100 kg, respectively.

Zinc yellow can be prepared by addition of sodium bichromate to a slurry of zinc oxide containing potassium chloride. Hydrochloric acid then is added for pH adjustment:

$$4\,ZnO + 2\,Na_2Cr_2O_7 + 2\,KCl + 2\,HCl + 2\,H_2O \rightarrow 4ZnO.K_2O.4CrO_3.3H_2O + 4\,NaCl \qquad (25)$$
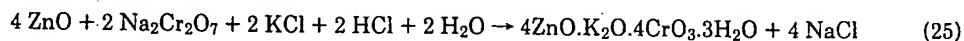
Zinc yellows with low chloride and sulfate content prevent blistering when used in coatings. The main use of zinc yellow is in the pigmentation of corrosion-inhibitive primers. Zinc yellow is a mild base. It and other chromate primer pigments are slightly soluble in water and release chromate ions which protect various ferrous and nonferrous metal surfaces. Chromate ion is an effective corrision inhibitor that increases the polarization of local anodes in the exposed area. For iron, this mechanism is the oxidation of ferrous ions to a continuous thin film of Fe_2O_3 which prevents dissolution of the iron and retards corrosion of the metal. It is important to maintain a sufficient inhibitor concentration. Excesses above the minimum do no harm, but insufficient chromate allows localized corrosion or pitting. Zinc yellow releases a chromate ion concentration of 1.276 g CrO_4^{2-}/L H_2O, compared to 0.58 g CrO_4^{2-}/L H_2O for a strontium chromate and 0.023 g CrO_4^{2-}/L H_2O for a basic zinc chromate.

Basic Zinc Chromate (Zinc Tetroxychromate). Basic zinc chromate is greenish yellow in masstone but is dirtier than zinc yellow. It is a weak pigment, is low in hiding power and, like zinc yellow, is nonbleeding in organic solvents. The density and oil absorption of basic zinc chromate is 3.87–3.97 and 46 g/100 g, respectively. The low

release of CrO_4^{2-} by basic zinc chromate makes it a more effective metal conditioner than a metal primer pigment. Therefore, it is used as a wash primer which promotes adhesion of finishes to metals, eg, steel, aluminum, and zinc. Basic zinc chromate is prepared directly by addition of chromic acid solution to a zinc oxide slurry:

$$5\,ZnO + CrO_3 + 4\,H_2O \rightarrow 4\,Zn(OH)_2 \cdot ZnCrO_4 \qquad (26)$$
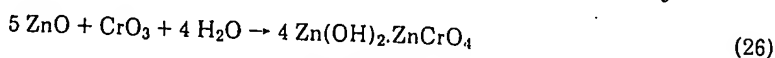
The resulting pigment is free of water-soluble chlorides and sulfates.

Strontium Chromate. Strontium chromates exhibit densities of 3.67–3.82 g/cm³. A low hiding strontium chromate has an oil absorption of 20 g/100 g whereas that of the regular type is 33 g/100 g. Strontium chromate, once used as an art pigment, finds use as a primer pigment for metal protection and corrosion resistance. It is used on aluminum and magnesium and their alloys and in vinyl sheeting. The pigment precipitates from the reaction of strontium nitrate and sodium chromate.

Red Lead. Red lead (98 wt %) has a density of 8.9 g/cm³, a refractive index of 2.42, and oil-absorption values of 7–10 g/100 g. The fume variety provides a higher degree of hiding than the furnace type. Red lead is prepared mainly by a furnace procedure or a fume procedure. Litharge is the starting material for furnace red lead. The charge is calcined for ca 24 h or longer, depending on the grade of red lead desired, at 454–482°C. Fumed red lead is prepared by first atomizing molten lead into fine particles and immediately flame-heating the particles to 1760–1816°C in an oxidizing atmosphere. The fumed product then is cooled and fine particles are produced.

The various grades of red lead depend on the minimum true red lead content. The grades are 85, 95, 97, and 98 wt % red lead and orange mineral. The 97 and 98 wt % red leads are the most common. The production volume and usage of mineral orange is small.

The primary use of red lead is as a metal-protective pigment on iron and steel surfaces. Red lead in combination with film-forming vehicles provides tough paint films which exhibit low moisture absorption and low penetration to vapors and fumes. The durability of the paint film results from the reaction of red lead with acidic compounds, eg, fatty acids in the vehicles, which leads to the formation of lead soaps that strengthen the films.

Cuprous Oxide. Cuprous oxide is incorporated in marine paints as an antifoulant pigment. Two grades of Cu_2O are available. Cuprous oxide has a density of 6 g/cm³ and a refractive index of 2.705. The red variety has a higher tinting strength than the purple grade. Both varieties have similar oil absorptions, 6–9 g/100 g.

Cuprous oxide is manufactured by an electrolytic process utilizing a caustic-doped solution of salt between copper electrodes. It also can be made by oxidation of metallic copper at 927–1038°C or by heating and decomposing precipitated copper compounds. Cuprous oxide also is used as a colorant for ceramic glazes and glasses.

Calcium Plumbate. Commercial calcium plumbate is cream colored with a density of 5.7 g/cm³. A typical product contains 94 wt % min calcium plumbate. It is prepared by the reaction of lime (CaO) and litharge (PbO) in the presence of oxygen at ca 700°C. The principal application of calcium plumbate is as an anticorrosion pigment for steel and galvanized steel.

Basic Lead Silicochromate. Basic lead silicochromate [11113-70-5] is comprised of a core of silica around which is a coating of gamma tribasic lead silicate and monobasic lead chromate. Two grades are sold and one is marketed for use in electrodeposition of water-base coatings for the auto industry. The pigment is manufactured by

preparing a slurry of litharge, silica, and catalytic amounts of acetic acid. Chromic acid is added and the mix is fed into a rotary kiln where, at first, tetrabasic lead chromate is formed. Increase of process temperatures induces further reaction and the formation of monobasic lead chromate and gamma tribasic lead silicate.

White Molybdates. White molybdate pigments, eg, calcium molybdate, $CaMoO_4$, strontium molybdate, $SrMoO_4$, and zinc molybdate, $ZnMoO_4$, are produced for use as corrosion inhibitors. These pigments were developed in ca 1960 and, in 1972, a basic zinc molybdate was patented (60). They are white, essentially nontoxic pigments prepared by precipitation techniques. Their properties are listed in Table 17. Zinc molybdate is sold as a pure pigment and in an extended form containing 25 wt % zinc molybdate.

Modified Barium Metaborate. Modified barium metaborate is a white pigment with a specific gravity of 3.25–3.35, a refractive index of 1.55–1.6, an oil absorption value of 30 kg/100 kg, and it contains a minimum of 90 wt % barium metaborate, $Ba_2O_4 \cdot H_2O$. Originally the pigment was developed and patented as a mold inhibitor for oleoresinous vehicles. It is a multifunctional pigment for paints which contributes, among other properties, package preservation, enzyme inhibition, corrosion resistance, and chalk resistance (61).

Zinc Phosphate. Zinc phosphate is a white pigment of low opacity, is nontoxic, and is used primarily in corrosion-resistant primers and undercoats for steel. Its specific gravity and oil-absorption values are 3.3 and 18–20 g/100 g, respectively. Poor opacity can be overcome by mixing the zinc phosphate with more opaque pigments. Zinc phosphate has been formulated successfully into a variety of vehicle binders, eg, chlorinated rubber, epoxy esters, and alkyds. One suggested mechanism for its corrosion resistance is the formation of a complex between iron and zinc phosphate (62). Chromium phosphate [13475-97-3], $CrPO_4 \cdot 3H_2O$, is another corrosion-inhibiting pigment.

Nacreous Pigments. Nacreous, ie, pearlescent, pigments are used for decorative effect. The original pearl essence pigments were derived from fish scales and tissue. Platelet crystals of purines, specifically guanine (2-amino hypoanthine or 2-amino-6-hydroxypurine) and hypoxanthine (6-hydroxypurine) were derived in varying ratios, with the major component being guanine from the scales and tissues (see Pigments, organic). Limited supplies of the natural resource led to the development of nacreous basic lead carbonate in the 1930s.

Important requirements for pearl essence are a platelike particle shape coupled with a high refractive index. Current pigment manufacture involves titanium dioxide- and iron oxide-coated mica. The mica provides the required transparent platelet base and the titanium dioxide and iron oxide provide the necessary refractive index.

Table 17. Properties of White Molybdate Pigments[a]

Pigment	Density, g/cm³	Oil absorption, g/100 g	Water solubility, g/L
calcium molybdate	4.2	12	0.05
strontium molybdate	4.6	20	0.02
zinc molybdate	4.5	16	4.5
zinc molybdate, basic	5.1	15	0.2

[a] Refs. 6–7.

Manufacture of titanium dioxide-coated mica involves precipitation of hydrous titanium dioxide by heating acidic solutions followed by calcination at 900°C to form the crystalline material on the mica platelet.

Basic lead carbonate and titanium dioxide mica can act as interference pigments. Although basically white or colorless, a change in the thickness of the platelets causes color effects and, as the thickness of the platelet is increased, a sequence of color hues can be achieved and repeated. Interference pigments display, transmit, and reflect color.

Metallics. The principal metallic pigments are prepared from metallic elements and their alloys, eg, aluminum, copper, bronze, and zinc. Minor use is made of metals and alloys, eg, tin, nickel, lead, gold, silver, and stainless steel. In 1866, a commercially practical aluminum smelting process was developed independently in France and in the United States (see Aluminum). Greater availability of aluminum led to its trial as a substitute for silver and tin powders.

A safe aluminum bronze powder manufacturing process was patented in the mid-1920s and was based on a wet ball mill procedure (63). The size reduction of aluminum is carried out with a lubricant-containing solution of paint thinner, mineral spirits. The physical properties of the pigment, the fineness or coarseness of the flake particles, the leafing and nonleafing characteristics, and the metal content of the packed-out paste depend on such factors as milling time and the type and amount of lubricants and mineral spirits used. The current manufacturing process involves the use of 99.5–99.97% pure aluminum. The aluminum is atomized to a powder form and is sized by screening so that it can be used as the feedstock for the flake. If a leafing aluminum flake is to be produced, stearic acid is used as the lubricant. For nonleafing types, a long-chain, unsaturated fatty acid, eg, oleic acid, is used. Stearic acid is not wetted easily by hydrocarbon solvents. The high interfacial tension between the solvent and the monomolecular layer of stearic acid which coats each flake causes the aluminum flakes to rise to the surface and to float, thereby forming an effective barrier against the penetration of moisture and corrosive fumes. In contrast to this, oleic acid lubricant is wetted easily by organic solvents and the aluminum flakes remain scattered throughout the body of the paint film. Therefore, nonleafing flake systems can be colored without being masked by the metallic flake. After being milled, the slurry of aluminum flakes is screened and filter-pressed to remove the milling lubricant. Clean solvent is added to the presscake to produce proper metal-to-solvent ratios for the pastes. The wet ball-mill process results in aluminum flakes of thicknesses of 0.13–0.8 μm. The covering power of the leafing flakes is very large as suggested by the fact that 1 g of aluminum flake powder, 0.2 μm thick and 10-μm diameter (avg) contains (1–2) $\times 10^{10}$ discrete aluminum particles (64).

Most aluminum flake pigment is sold in a paste form which, typically, contains 65 wt % flake metal and 35 wt % volatile hydrocarbon. Powder forms are used where the formulation vehicle is incompatible with the mineral spirits or solvent of the paste preparation. Many grades are marketed for leafing and nonleafing types (see Table 18). Leafing grades can be modified by polishing, which results in high luster; burnished types are marketed at 74 wt % aluminum flake loadings. The available average particle size of the nonleafing aluminum pigments varies more widely than that of the leafing types, because particle-size distribution is controlled more closely with the former since size variation has a considerable effect on appearance.

Bronze pigments or powders are manufactured from granular alloys of copper

Table 18. Types and Applications of Aluminum Flake Pigments

Type	Covering, cm^2/g	Surface area, m^2/g	Application
leafing			
coarse	9,000–16,000		bright industrial paints, asphalt roof coatings
medium	14,000–26,000		industrial maintenance paints, heat-resistant paints
fine	28,000–32,000		metallic decorative enamels, artists colors and lacquers
nonleafing			
coarse		1.0–5.5	polychrome paints, colored roof coatings
medium		6.5–8.6	can coatings, maintenance paints, polychrome paints
fine		10.5–13.0	can coatings, product finishes

and zinc. Varying the copper and zinc ratio produces color changes in the pigments. At 100 wt % Cu, the color is red to pink; at 90 wt % Cu–10 wt % Zn, the pigment is a pale gold; at 80 wt % Cu–20 wt % Zn, the color is rich gold; and at 70 wt % Cu–30 wt % Zn, the color is green–gold. In some formulations, a small amount of aluminum is introduced. Bronze powders are used widely in coating paper and cardboard as well as in paints, plastics, and printing inks.

Zinc Dust. Metallic zinc powder or dust is gray and the pigment particles are round. Zinc dust has a density of 7.0–7.1 g/cm^3, oil absorption of 5–20 g/100 g, and particle sizes of 1–44 μm with an average size of 3–8 μm. Zinc dust is prepared with a minimum of 97.5 wt % zinc, and is manufactured by vaporizing zinc in electrothermic furnaces, followed by shock cooling, which causes condensation of the zinc into spherical droplets. Particle size is controlled by the rate of cooling. The zinc dust is conveyed from the bottom of the cooling chamber to screens for classification. The presence of a minimum of oxygen during manufacture prevents formation of zinc oxide. In 1977, 43,177 t of zinc dust was produced in the United States, at an average value of $1.05/kg (65).

Zinc dust is a widely used pigment on iron and steel because of its cathodic protection effect. Zinc-rich paints are prepared with chlorinated rubber, epoxy ester, polyurethane, polyester, and inorganic vehicles, eg, alkyl silicates and alkali-metal silicates.

Luminescent Pigments. Luminescent pigments are based largely on zinc sulfide and zinc–cadmium sulfide which are doped with an activating material, eg, silver, copper, or manganese, to the extent of 0.033–1.0 wt %. These pigments are slightly coarser than the metallic pigments and are either colorless or have pastel shades. Depending on the activator, under uv radiation a wide spectrum of colors can be obtained, eg, blue, green, yellow, orange, and red. Some important properties of these pigments are chemical stability, brightness, and persistence. Persistence relates to the activation of the pigment and is relatively short for the fluorescent type under uv excitation and long for the phosphorescent type which, during exposure to daylight, uv, etc, stores energy and releases it as visible light. Luminescent inorganic pigments are nonradioactive (see Luminescent materials).

Primary application areas for these pigments are indoor decoration, safety signs,

television and electronics, and military coatings. The pigments should be protected from severe exposure, eg, to direct sunlight and moisture, which may deteriorate pigment properties.

Nomenclature

CIE = International Commission on Illumination (Commission internationale de l'éclairage)
BET = Brunauer-Emmett-Teller

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ORGANIC

Pigments are colored, colorless, or fluorescent particulate solids that usually are insoluble in and essentially are physically and chemically unaffected by the vehicle or medium in which they are incorporated. They alter appearance either by selective absorption or by scattering of light. Pigments may be organic or inorganic chemicals. They usually are dispersed in vehicles for application, eg, in inks (qv) or paints (see Paint). In some cases, the substrate may serve as a vehicle, eg, in the mass coloration of a polymeric material (see also Colorants).

Pigments and dyes differ in solubility characteristics and in the method of application (see Dyes, evaluation and application). When a pigment is used to color or opacify a substrate, the finely divided, insoluble solid remains insoluble throughout the coloration process. Flavanthrone [475-71-8] behaves as either a yellow dye or pigment.
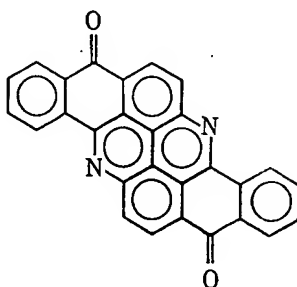
flavanthrone

As a pigment, flavanthrone is a particulate, insoluble solid and is dispersed directly

into a vehicle, eg, oil or plastic. Such a dual-function compound is characterized by one Colour Index (CI) number but two CI names, depending on application, eg, CI 42040: Basic Green 1 or Pigment Green 1.

Commercially significant organic pigments are listed in Table 1.

Prior to the discovery of Perkin's Mauve [6373-22-4] in 1856, color was obtained from natural sources, eg, madder, indigo, cochineal, and logwood (see Dyes, natural). The development of synthetic coloring matters followed with the discovery of Fuchsine [632-99-5] in 1858 and of other triphenylmethane dyes, eg, Alkali Blue, Methyl Violet, and Malachite Green (see Triphenylmethane and related dyes). Lakes of these dyes were used as the first synthetic organic pigments.

The initial synthetic developments were concerned principally with dyestuffs for the textile industry, and the period up to the early 1900s was characterized by the discovery and development of many dyes derived from coal-tar intermediates (see Dyes and dye intermediates). Rapid advances in color chemistry were initiated by the discovery of diazo compounds and of azo derivatives (see Azo dyes). The color potential of this class of compounds and their ease of preparation led to the development of azo colors, which represent the largest fraction of organic pigments. Azo dyes for pigment use, ie, azo-pigment dyes, became significant commercially with the discovery of the Lithol Reds in 1899 (1).

Many late nineteenth-century U.S. pigment manufacturers produced dyestuff-derived lakes, eg, Peacock Blue, Persian Orange [633-96-5], yellow lakes, and scarlets. Such synthetic products generally replaced the natural products because of the formers' superior characteristics, including uniformity, intensity or brilliance of shade, and resistance to light and other chemical and physical agents.

Among the first pigments produced in the United States subsequent to World War I were Phloxine Red [1326-05-2] (see Xanthene dyes) and Peacock Blue. The first synthetic azos included Toluidine Red, Lake Red C, Para Red, Hansa Yellow, and Lithol Red.

The development in 1913 of the brilliant lakes of complex heteropoly acids of phosphorus, molybdenum, and tungsten with basic dyes, eg, Rhodamine [81-88-9], Victoria Blue, and Methyl Violet, led to the production of pigments with fastnesses that were superior to the tannin tartar emetic precipitations of the same dyes. These products, however, were deficient in their resistance to solvents and alkali and were not sufficiently durable for outdoor use. The largest single advance in pigment technology after World War I and prior to 1933 was the discovery of the phthalocyanines (see Phthalocyanine compounds). These blue and green pigments were characterized by excellent intensity, strength, bleed resistance, and lightfastness.

Color and Constitution. Color in organic compounds is associated with the presence of multiple bonds; the groups responsible for color are chromophores. The unsaturated, conjugated double bonds in chromophores contribute to the selective absorption of visible light. Chromophores that are common in colored organic materials include
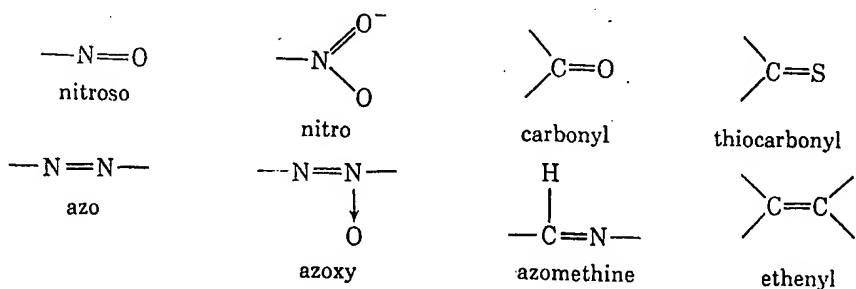
Table 1. Selected Commercial Synthetic Organic-Pigment Toners and Lakes

CI name	CAS Registry Number	CI number	CAS Registry Number	Common name	Coupling components	
					First	Second
Pigment Blue 1	[1325-87-7]	42595	[2390-60-5]	Victoria Pure Blue BO		
Pigment Blue 2	[1325-94-6]	44045	[2580-56-6]	Victoria Blue B		
Pigment Blue 9	[1325-74-2]	42025	[3521-06-0]	Setaglaucine, Rhoduline Blue 6G		
Pigment Blue 14	[1325-88-8]	42600	[2390-59-2]	Ethyl Violet		
Pigment Blue 15, alpha, beta forms	[147-14-8]	74160	[147-14-8]	Phthalocyanine Blue		
Pigment Blue 19	[58569-23-6]	42750A	[58569-23-6]	Alkali Blue		
Pigment Blue 24	[6548-12-5, 14940-82-0]	42090	[2650-18-2]	Peacock Blue		
Pigment Blue 25	[10127-03-4]	21180	[10127-03-4]	Dianisidine and Naphthol AS		
Pigment Green 1	[1325-75-3]	42040	[633-03-4]	Brillant Green		
Pigment Green 2	[12213-70-6]	42040 and 49005	[2390-54-7]	Brillant Green and Thioflavine T		
Pigment Green 4	[1325-72-0, 61725-50-6]	42000	[569-64-2]	Malachite Green		
Pigment Green 7	[1328-53-6]	74260	[1328-53-6]	Phthalocyanine Green		
Pigment Green 36	[14302-13-7]	74265	[14302-13-7]	copper polybromochloro-phthalocyanines		
Pigment Orange 5	[3468-63-1]	12075	[3468-63-1]	Dinitraniline Orange	2,4-dinitroaniline	2-naphthol
Pigment Orange 13	[3520-72-7]	21110	[3520-72-7]	Pyrazolone Orange	3,3'-dichlorobenzidine	3-methyl-1-phenyl-2-pyrazolin-5-one
Pigment Orange 16	[6505-28-8]	21160	[6505-28-8]	Dianisidine Orange	o-dianisidine	acetoacetanilide
Pigment Orange 34	[15793-73-4]	21115	[15793-73-4]	Pyrazolone Orange or Tolyl Orange	3,3'-dichlorobenzidine	3-methyl-1-p-tolyl-2-pyrazolin-5-one
Pigment Red 1	[6410-10-2]	12070	[6410-10-2]	Para Red	p-nitroaniline	2-naphthol
Pigment Red 2	[6041-94-7]	12310	[6041-94-7]	Naphthol Red or Permanent Red FRR	2,5-dichloroaniline	Naphthol AS
Pigment Red 3	[2425-85-6]	12120	[2425-85-6]	Toluidine Red	2-nitro-4-methylaniline	2-naphthol
Pigment Red 4	[2814-77-9]	12085	[2814-77-9]	Chlorinated Para Red	2-chloro-4-nitroaniline	2-naphthol

Pigment Red 5	[6410-41-9]	12490	[6410-41-9]	Naphthol Red or Permanent Carmine FB	N,N-diethyl-4-methoxy-metanilamide	Naphthol AS-ITR
Pigment Red 17	[6655-84-1]	12390	[6655-84-1]	Naphthol Red M	5-nitro-2-methylaniline	Naphthol AS-D
Pigment Red 18	[3564-22-5]	12350	[3564-22-5]	Toluidine Maroon	2-nitro-p-toluidine	Naphthol AS-BS
Pigment Red 22	[6448-95-9]	12315	[6448-95-9]	Naphthol Red L	5-nitro-2-methylaniline	Naphthol AS
Pigment Red 23	[6471-49-4]	12355	[6471-49-4]	Naphthol Red B	5-nitro-2-methoxyaniline	Naphthol AS-BS
Pigment Red 38	[6358-87-8]	21120	[6358-87-8]	Pyrazolone Red	3,3'-dichlorobenzidine	5-oxo-1-phenyl-2-pyrazoline-3-carboxylic acid ethyl ester
Pigment Red 48 barium, calcium, strontium, and manganese salts	[7585-41-3, 7023-61-2, 15182-05-5, and 5280-66-0]	15865	[3564-21-4]	Permanent Red 2B	6-amino-4-chloro-3-methylbenzenesulfonic acid	3-hydroxy-2-naphthoic acid
Pigment Red 49 barium and calcium salts	[1103-38-4 and 1103-39-5]	15630	[1248-18-6]	Lithol Red R	2-amino-1-naphthalene-sulfonic acid	2-naphthol
Pigment Red 52 calcium	[17852-99-2]	15860	[5858-82-2]	Lithol Red 2G[a]	2-amino-5-chloro-4-methylbenzenesulfonic acid	3-hydroxy-2-naphthoic acid
Pigment Red 53	[5160-02-1]	15585	[2092-56-0]	Lake Red C	2-amino-5-chloro-4-methylbenzenesulfonic acid	2-naphthol
Pigment Red 57	[5281-04-9]	15850	[5858-81-1]	Lithol Rubine B	6-amino-m-toluenesulfonic acid	3-hydroxy-2-naphthoic acid
Pigment Red 60	[1325-16-2]	16105	[1836-22-2]	Pigment Scarlet 3B	anthranilic acid	2-naphthol-3,6-disulfonic acid
Pigment Red 63	[6417-83-0, 21416-46-6]	15880	[35355-77-2]	BON Maroon	2-amino-1-naphthalene-sulfonic acid	3-hydroxy-2-naphthoic acid
Pigment Red 81 PMA, PTA tones[b]	[12224-98-5, 57449-56-6]	45160	[989-38-8]	Rhodamine 6G		
Pigment Red 83	[72-48-0]	58000	[72-48-0]	Alizarine Red B		
Pigment Red 90	[17372-87-1]	45380	[17372-87-1]	Bromo Acid or Eosin		
Pigment Violet 1	[1326-03-0]	45170	[81-88-9]	Rhodamine B		
Pigment Violet 3	[1325-82-2]	42535	[8004-87-3]	Methyl Violet B		
Pigment Violet 5	[145-48-2]	58055	[145-48-2]	Helio Fast Rubine 4BL		
Pigment Violet 19	[1047-16-1]	46500	[1047-16-1]	Quinacridone		
Pigment Violet 23	[6358-30-1]	51319	[6358-30-1]	Carbazole Dioxazine Violet		
Pigment Yellow 1	[2512-29-0]	11680	[2512-29-0]	Hansa Yellow G	2-nitro-p-toluidine	acetoacetanilide

Table 1 (*continued*)

CI name	CAS Registry Number	CI number	CAS Registry Number	Common name	Coupling components	
					First	Second
Pigment Yellow 3	[6486-23-3]	11710	[6486-23-3]	Hansa Yellow 10G	4-chloro-2-nitroaniline	o-chloroacetoacetanilide
Pigment Yellow 12	[6358-85-6]	21090	[6358-85-6]	Diarylide Yellow GR	3,3'-dichlorobenzidine	acetoacetanilide
Pigment Yellow 13	[5102-83-0]	21100	[5102-83-0]	Diarylide Yellow MX	3,3'-dichlorobenzidine	acetoacet-2,4-dimethylanilide
Pigment Yellow 14	[5468-75-7]	21095	[5468-75-7]	Diarylide Yellow OT	3,3'-dichlorobenzidine	o-acetoacet-o-toluidide
Pigment Yellow 17	[4531-49-1]	21105	[4531-49-1]	Diarylide Yellow OA	3,3'-dichlorobenzidine	o-acetoacetanisidide
Pigment Yellow 73	[12225-12-6]	11738	[13515-40-7]		2-nitro-4-methoxyaniline	acetoacet-o-anisidide
Pigment Yellow 74	[6358-31-2]	11741	[6358-31-2]		4-nitro-2-methoxyaniline	acetoacet-o-anisidide
Acid Red 26	[3761-53-3]	16150	[3761-53-3]	Scarlet 2R	2,4-xylidine	2-naphthol-3,6-disulfonic acid

[a] Lithol Red 2G generally is accepted as the name for Pigment Red 52, although in the Colour Index, the name is listed as Pigment Red 69.
[b] In this context, the abbreviation PTA is phosphotungstic acid and phosphotungstomolybdic acid. The notation PMA indicates phosphomolybdic acid.

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Chemical groups that play an auxiliary function by intensifying or modifying color are auxochromes. The greater the extent or degree of conjugation in the molecule, the deeper the color reflected; the dominant absorption band in the visible portion of the spectrum undergoes a bathochromic shift, ie, to longer wavelengths. A hypsochromic shift involves the dominant absorption moving to shorter wavelengths. The incorporation of chemical groups that participate in the resonating system enhances color development. Some typical auxochrome groups are

$$-N\overset{\displaystyle H}{\underset{\displaystyle H}{<}} \qquad -N\overset{\displaystyle H}{\underset{\displaystyle CH_3}{<}} \qquad -N\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{<}} \qquad -OCH_3 \qquad -OH$$

amino   alkylamino   dialkylamino   methoxy   hydroxy
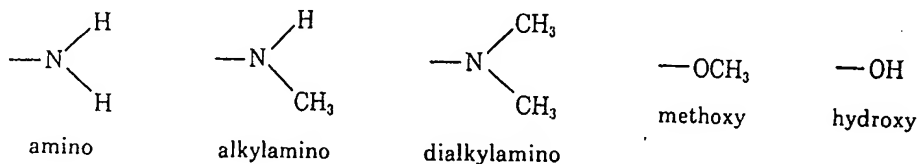
Polymorphism also can produce differently colored crystalline forms, eg, quinacridone exhibits red and violet polymorphic forms.

The color of an organic pigment depends on the selective absorption of portions of visible light, ie, light with wavelengths of ca 400–750 nm, and the consequent reflection of all that is not absorbed (see Table 2). Often a mixture of different chromophore types in a molecule results in dullness because absorption occurs over a wide spectral range, which represents the composite of the absorption characteristics of each of the chromophore types (see also Color).

Properties

The physical and chemical characteristics that control and define the performance of a commercial pigment in a vehicle system include its chemical composition; chemical and physical stability; solubility; particle size and shape; degree of dispersion or aggregation; crystal geometry; including polymorphic crystalline form; refactive index; specific gravity; absorption in the visible, uv, and ir regions of the spectrum; extinction coefficients; surface area; surface character; and the presence of impurities, extenders, or surface-modifying agents. Almost invariably a pigment is used in a vehicle system, so that ultimate performance in use derives from a physical or chemical pigment–vehicle interaction in a specific vehicle system.

Table 2. Absorption Wavelength and Color

Wavelength, nm	Absorbed	Visible
400–435	violet	yellow–green
435–480	blue	yellow
480–490	green–blue	orange
490–500	blue–green	red
500–560	green	purple
560–580	yellow–green	violet
590–595	yellow	blue
595–605	orange	blue
605–750	red	blue–green

Strength. The inherent strength of a pigment is controlled by its light-absorbing properties, which are related to its molecular and crystalline structure. The inherent strength of a pigment seldom is obtained in practical application but is compromised by considerations of particle size and exposed surface area which, in turn, are controlled by the degree of dispersion, aggregation, flocculation, etc. Pigment strength in a vehicle also is determined by the optical character of the other constituents in the pigmented system insofar as they absorb or scatter light. For maximum practical strength and the development of full tinctorial properties, a dry pigment usually must be dispersed in a vehicle by application of work, often by attrition, to break up the dry-pigment aggregates and to obtain maximum wetting by the vehicle. Some chromophores have greater inherent strength than others, eg, the diazo pigment Diarylide Yellow is approximately twice as strong as the monoazo Hansa Yellow.

Intensity. The intensity of a colored pigment is a measure of its brightness or cleanness, as opposed to dullness, of hue. Dullness may be visualized in terms of the amount of gray or black in the color. Generally, a pigment with a molecular structure that reveals two or more chromophores is more likely to be less intense than one containing a single chromophore. A pigment color that reflects visible light over a wide band of wavelengths or in several wavelength bands probably is less intense than a similarly hued color that reflects over a narrow wavelength band or in a single band. The intensity of a blend of pigments is altered by the selective absorption of the different pigments in the blends, and this significantly controls the intensity of the reflected color. An intense pigment color exhibits great clarity and provides flexibility in color blending, and its use offers important economic advantages since blending with duller and less-expensive pigments, eg, carbon black [1333-86-4] or earth colors, such as, iron oxides, is facilitated.

Fastness. The fastness of a colored pigment defines its inherent ability to withstand the chemical and physical factors to which it is exposed during and subsequent to its incorporation into the pigmented system and in its ultimate application. Fastness describes the behavior of a pigment in terms of retaining its initial color value, either alone or as a component of a pigmented system on exposure to light, weather, heat, solvents, or chemicals. Ideally, a pigment should be chemically inert. Although few synthetic organic pigments show such perfection, some, eg, carbon black, approach it. The fastness requirements for pigments have become increasingly stringent because of the proliferation of pigment vehicles fostered by the introduction of synthetic media, eg, resins, plastics, fibers, lacquers, enamels, printing-ink vehicles, elastomers, molding resins, etc. The use of plasticizers, curing agents, more potent solvents, and higher operating and curing temperatures has made many pigments that previously were acceptable in oleoresinous systems unusable in the newer systems.

Pigment durability defines the pigment's ability to withstand the combined chemical and physical agencies inherent in weather, eg, light, temperature, water, gases, industrial effluents. Ultimately, the total pigmented system must meet the requirements of durability because each component may interact with the others: the pigment may be responsible for the deterioration of the film or the vehicle may contribute to the deterioration of the pigment. A given pigment may perform as a lightfast pigment in one system and fail in lightfastness in another.

The quantitative expression of lightfastness is difficult because of variable lightfastness performance under different conditions, eg, the chemical nature of the vehicle, the presence of other pigments and extenders, variable conditions of exposure,

and the concentration at which the pigment is exposed. There are no commonly accepted numerical standards for lightfastness nor standard conditions for carrying out such tests.

Heat stability may be affected either by the chemical or physical factors incident to the use of temperatures such as may be applied during the incorporation of the pigment into the vehicle, eg, in the manufacture of vinyl sheet, high temperature extrusion of plastics, or high temperature baking of automotive and industrial finishes. However, high temperature conditions also may be encountered under use conditions.

Heat and color instability also result from melting, sublimation, change in crystal form, or the variable solubility of the pigment in a vehicle as a function of temperature, insofar as the dissolved color shade differs tinctorially from that of the particulate, dispersed, solid color. Under these conditions, the hue of colored plastic varies with the extrusion temperature of the plastic.

Fastness also includes resistance to bleeding which is dependent of the solubility of the pigment in the vehicles, plasticizers, and solvents to which it is exposed. Bleeding may occur during pigment incorporation; during application of the pigmented system, eg, in a coating process; or during use of the pigmented system. Pigment solubility may be apparent in the case of pigment transfer or migration from one pigmented surface to another, eg, when colored vinyl sheets are pressed together or when a paint film is applied over another differently colored film.

The solvent, plasticizer, and vehicle types to which pigments may be exposed include alcohols; aromatic and aliphatic hydrocarbons, eg, paraffin wax; ketones; ether alcohols; acids, eg, oleic acid; soap formulations; cellulose nitrate, ie, nitrocellulose; acrylic lacquers; linseed oil; and numerous synthetic resins.

Chemical fastness is the resistance of the pigment in the pigmented vehicle principally to agents, eg, acids or alkali, or to air contaminants, eg, hydrogen sulfide. For example, cleansing a pigmented coating with soap, detergent, or bleaching agents requires such resistance. Specialized uses, eg, paint for swimming pools, requires resistance to alkaline hypochlorite.

Dispersibility. The dispersibility of a pigment is measured by the effort required to develop the full tinctorial potential of a pigment in a vehicle system (see Pigments, dispersed). For a given pigment, dispersibility varies from vehicle to vehicle in terms of the dependence of wetting, flocculation, etc, on the interaction of pigment and vehicle. Other attributes of the pigment, eg, aggregation, may make the use of a pigment impractical in any system unless the aggregates are broken up. Aggregation arises from forces of attraction between the discrete pigment particles and from physical bridging between particles as a result of solvent action and crystallization, which may occur during pigment drying.

Dispersibility affects the maximum surface area and homogeneity of the pigmented system; the latter affect the value per unit weight of pigment and improved properties, eg, gloss and transparency, in certain system applications.

Texture often describes ease of dispersion, ie, a hard pigment texture requires greater effort on the part of the user if an acceptable degree of dispersion is to be achieved. Use of special extenders and surface-active agents, as well as other techniques, improve the texture and compatibility of pigments in most vehicle systems. However, the attainment of one useful property in a pigment may compromise another. For example, the achievement of transparency in an automotive paint is accomplished

primarily by the development of small particles; however, the latter cause greater aggregation with resulting texture and dispersion problems, so that a compromise in properties may be necessary.

Working Properties. Working properties of a pigment facilitate its incorporation, handling, or use in a given system. They include compatibility, oil absorption, contribution to rheology, ease of grinding, wettability, gloss, bronzing, hiding power, flocculation, etc. The pigment working properties are controlled during manufacture and during formulation by the pigment user. From a practical point of view, a pigment need be no more durable than the vehicle or film in which it is used nor more durable or possess other properties than are demanded by the use for which it is intended.

Organic- and Inorganic-Pigment Properties. The general properties that, with exceptions, characterize the organic as compared to the inorganic pigments are as follows.

Solubility. Inorganic pigments generally are insoluble, ie, nonbleeding, in organic solvents; however, many organic pigments show slight solubility in these solvents.

Tinctorial Strength. Generally, organic pigments are characterized by greater tinctorial strength.

Hiding Power. Inorganic pigments usually are opaque, in contrast with the more transparent organic pigments.

Specific Gravity. The organic pigments generally exhibit lower specific gravity than the inorganic pigments.

Heat Resistance.. The organic pigments generally are less heat-resistant than the inorganic pigments.

Intensity. The organic pigments usually exhibit greater brightness.

Types

Organic pigments may be classified as azo or nonazo pigments. Azo pigments are formed by successive diazotization and coupling. A primary aromatic amine, which usually is referred to as the first component, dissolves or is suspended in a dilute mineral acid. Sodium nitrite is added, and the nitrous acid that forms reacts with the amine to yield the diazonium salt. The reaction usually occurs at low temperatures. Coupling is effected by the reaction of a solution or suspension of the second component with the unisolated diazonium salt. Examples of second components include 2-naphthol, 3-hydroxy-2-naphthoic acid, arylides or arylamides of 3-hydroxy-2-naphthoic acid, arylides of acetoacetic acid, and pyrazolone derivatives. The temperature, pH, rates of addition, presence of auxiliary agents, and agitation can affect the tinctorial and other pigmentary properties of the product.

The monoazo and disazo pigments contain, respectively, one and more than one chromophore (—N=N—) groups and are subdivided for convenience into two types, ie, the pigment dyes and the precipitated azos. Pigment dyes include products that are insoluble in the aqueous reaction medium directly on formation and, hence, require no metal ions or other means to effect precipitation, eg, toluidine reds, para reds, arylide reds and maroons, and Hansa and azo yellows. Precipitated azos include products containing salt-forming groups, principally sulfonic acid or carboxylic acid, which precipitate. The salts most commonly used for the precipitation include those of calcium, barium, strontium, and manganese. Among the precipitated pigments are Lithol Red, Maroon, and Rubine; Lake Red C; Pigment Scarlet; and Azo Bordeaux.

Characteristic properties of azo pigments are partial solubility in organic solvents and vehicles, poor bleed resistance, good acid and alkali resistance, good lightfastness in deeper shades, and poor tint lightfastness. Properties that characterize precipitated azos are good-to-excellent bleed resistance, poor acid and alkali resistance, fair to good lightfastness in deeper shades, and poor tint lightfastness.

Azo Yellows. *Hansa Yellows.* Hansa Yellows are monoazo pigments; a representative Hansa Yellow is Hansa Yellow G:
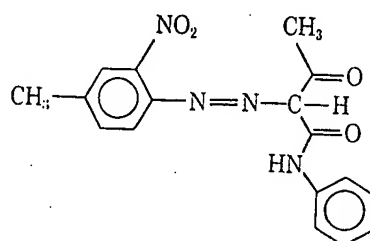
Hansa Yellow G   [12688-94-7]

The Hansa Yellows have been prepared in red to green shades and some of the commercially more important ones are formed by couplings, as shown in Table 3, in order of increasing greenness.

The Hansa Yellows are intense pigments and exhibit high tinting strength, good lightfastness in dark shades, ie, masstone, but poor tint lightfastness. Hansa Yellow G is particularly lightfast in masstone. The Hansa Yellows are semiopaque. Although they bleed in most paint solvents, they are resistant to alkali and acids. The Hansas are sensitive to heat and evidence high oil absorption. Their tinctorial strength is less than that of the diarylide yellows, which are disazo pigments, but greater than that of the inorganic chrome yellows. The Hansas are used extensively in emulsion paints, paper-coating compositions, and in paints requiring the use of lead-free pigments.

Diarylide Yellows. The formula for a typical diarylide yellow is that for Diarylide

Table 3. Hansa Yellows

Hansa Yellow (CI name and number)	CAS Registry No.	First component	Second component
R (Pigment Yellow 10, CI 12710)	[6407-75-6]	2,5-dichloroaniline	3-methyl-1-phenyl-5-pyrazolone
GR (Pigment Yellow 2, CI 11730)	[6486-26-6]	4-chloro-2-nitroaniline	acetoacet-*m*-xylidide
G (Pigment Yellow 1, CI 11680)	[2512-29-0]	2-nitro-*p*-toluidine	acetoacetanilide
5G (Pigment Yellow 5, CI 11660)	[4106-67-6]	2-nitroaniline	acetoacetanilide
10G (Pigment Yellow 3, CI 11710)	[6486-23-3]	4-chloro-2-nitroaniline	*o*-chloroacetoacetanilide

Yellow GR:
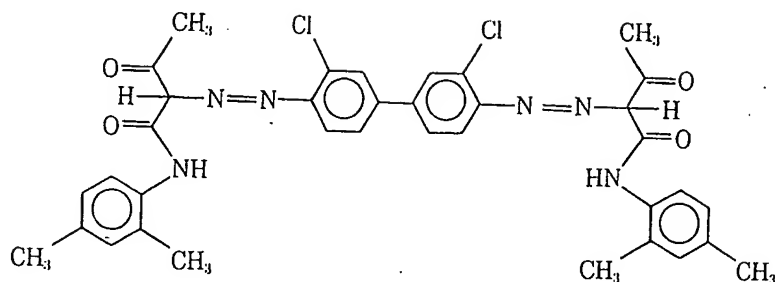
Diarylide Yellow GR (Pigment Yellow 13) [5102-83-0]

The same chemistry is involved as with the Hansa Yellows except that the first component amine is a disubstituted diaminobiphenyl which, upon diazotization, yields two diazonium-salt groupings. The latter couples with two molecules of the second component to yield the disazo yellow.

Generally, the intense yellows provide greater tinctorial strength and superior resistance to bleeding and heat than the Hansa Yellows. The former exhibit minimum bleeding in alcohol, water, and paraffin wax. However, they generally are inferior to the Hansas in lightfastness: dark shades of the intense yellows provide good lightfastness but poor tint lightfastness. They exhibit good chemical and bake resistance, low hiding, and high oil absorption.

Nickel Azo Yellow. Nickel Azo Yellow (Pigment Green 10, CI 12775) is a greenish yellow, chelated nickel azo pigment; is superior in permanence to any other azo yellow pigment; offers excellent lightfastness in masstone, tint, and metallic formulations; and provides good bake resistance. The product is the nickel chelate of the azo dye and is derived from the coupling of diazotized 4-chloroaniline and 2,4-dihydroxy-quinoline:
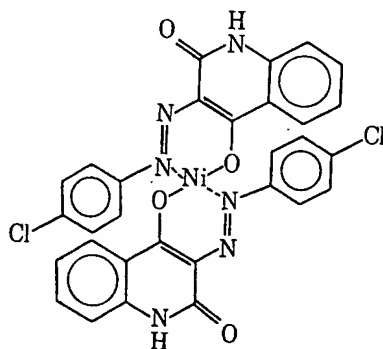
Nickel Azo Yellow [51931-46-5]

The nickel forms a coordinate bond with the azo nitrogen. Although chemically resistant, it is subject to demetallization under highly acid or alkaline conditions, which results in color drift, poor lightfastness, and solvent bleeding. The pigment provides excellent transparency which, with its superior durability, has resulted in its wide acceptance by the automotive finishes industry.

Azo Oranges. **Hansa Orange.** Hansa Orange (Pigment Orange 1, CI 11725) (Orange 3G) is an intense, high strength color of good lightfastness in dark shades and good chemical resistance. It has low hiding power and poor tint lightfastness and bleed resistance, and it is sensitive to heat.
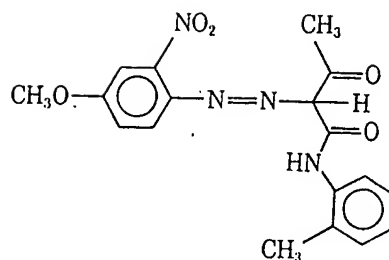
Hansa Orange [3819-14-5]

Dinitraniline Orange. Dinitraniline Orange (Pigment Orange 5) is an intense, high strength pigment and is superior in the latter respect to the inorganic molybdate orange which it approximates in masstone shade. It provides low hiding power, good light-fastness in dark shades, and poor tint lightfastness. Although chemically resistant, it is characterized by poor bleed resistance and only fair bake resistance.
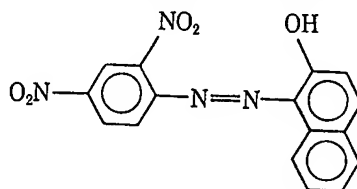
Dinitraniline Orange [3468-63-1]

Pyrazolone Orange. Pyrazolone Orange (Pigment Orange 13) is a disazo pigment and an intense color of high strength, with good lightfastness in dark shades but poor tint lightfastness. It is characterized by good bake and chemical resistance but provides low hiding and fair bleed resistance.
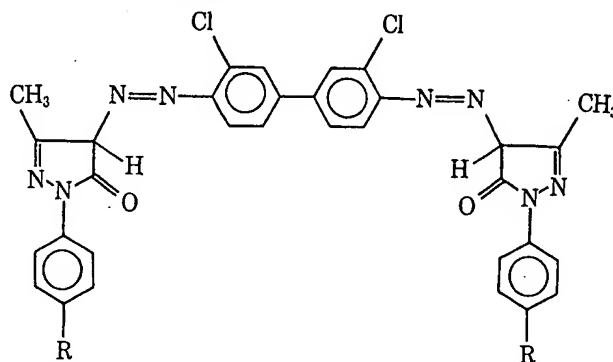
Pyrazolone Orange (Pigment Orange 13) R=H [3520-72-7]

Azo Reds and Maroons. **Toluidine Reds.** Toluidine Red (Pigment Red 3) is one of the most popular red pigments for industrial enamels. The highly intense azo-pigment dye provides excellent masstone lightfastness but poor tint lightfastness. It exhibits good bake and chemical resistance and good hiding power, but it shows poor bleed resistance in many solvents. Toluidine Reds of several different shades are available, but they are being displaced by other durable reds.
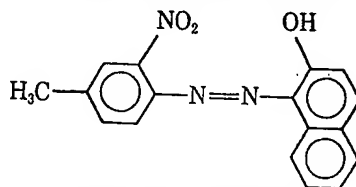
Toluidine Red [2425-85-6]

Para Reds.   Para Red (Pigment Red 1) is a low cost, intense red, which provides good hiding and chemical resistance. Lightfastness, especially in tints, is poor, as is bleed and bake resistance. The Para Reds are darker and bluer than the Toluidine Reds and are less lightfast.
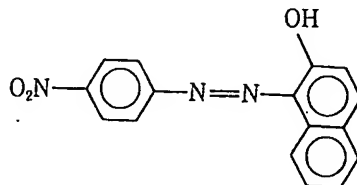
Para Red [6410-10-2]

The two commercially significant Para Reds are the lighter and yellower Para Red Y [6410-10-2] and the darker and bluer Para Red B [6410-10-2]. The latter is obtained by substituting a portion of 2-naphthol with an accessory agent. The use of Para Reds is severely limited by very poor bleed resistance.

Chlorinated.   There are two types of chlorinated Para Red: Pigment Red 4 and Pigment Red 6 (Parachlor Red, CI 12090). The first component of the latter is *p*-chloro-*o*-nitroaniline.
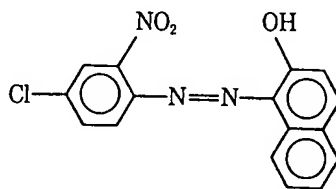
Pigment Red 6 [6410-13-5]

The chlorinated Para Reds are intense, very light yellowish red. Parachlor Red is significantly superior in both tint and masstone lightfastness to the *o*-chloro-*p*-nitroaniline product; its lightfastness is excellent in dark to medium shades and good in light shades. It is more transparent than the *o*-chloro isomer, which provides good hiding. Both isomers exhibit poor bleed and bake resistance. Parachlor Red is characterized by good chemical resistance and is one of the most lightfast of the azo pigment dyes.

Lithol Reds.   The Lithol Reds (Lithol Red R; Pigment Red 49) are among the more important of the precipitated azo-pigment dyes. They comprise a family of the sodium, barium, calcium, and strontium salts of the coupling product from diazotized Tobias acid or 2-naphthylamine-1-sulfonic acid and 2-naphthol. Intense reds of increasingly dark shades are obtained by using the metals in the order Na, Ba, Ca, Sr; barium and calcium salts are the most popular. The structure of the barium pigment is
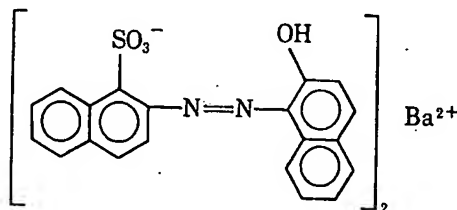
2-[(2-hydroxy-1-naphthalenyl)azo]-1-naphthalenesulfonic acid, barium
salt (2:1) [1103-38-4]

The Lithol Reds are used widely where intensity, hiding power, bleed resistance, and low cost are of primary importance. They generally are poor in lightfastness and are not satisfactory for outdoor use. Typical of precipitated azo dyes, they exhibit poor chemical and bake resistance. Lithol Reds are the most economical of the organic red and maroon pigments and are used widely where good durability is not required.

BON Reds and Maroons. The BON Reds and Maroons derive their name from the use of β-oxynaphthoic acid (BON or BONA) as the second component in the coupling of various diazotized amines containing salt-forming groups. Insolubilization is effected by metal ions, eg, calcium, barium, or manganese, and the shades vary from toluidine red to dark maroon.

Lithol Rubine. Lithol Rubine (Pigment Red 57) is the calcium salt of diazotized 2-amino-5-methylbenzenesulfonic acid coupled to 3-hydroxy-2-naphthoic acid.
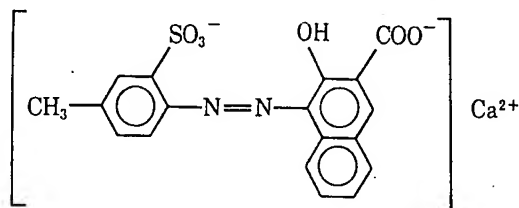
Lithol Rubine [5858-81-1]

It is dark red and usually is resinated, which enhances the intensity and depth of color. Lithol Rubine is characterized by good organic-solvent bleeding and bake resistance but poor alkali and soap resistance. Although it has poor lightfastness in blends with molybdate orange, it exhibits a wide range of intense shades suitable for interior industrial enamels. As a self-color, it is used where a high degree of exterior durability is not required. Because it provides cleaner, more intense print tones than Lithol Reds, it is used extensively in oil, gravure, and flexographic inks.

Permanent Red 2B. Permanent Red 2B (Pigment Red 48) defines the calcium, strontium, barium, and manganese precipitations of the coupling from diazotized 2-chloro-4-aminotoluene-5-sulfonic acid with 3-hydroxy-2- naphthoic acid. The first three are intense pigments and exhibit excellent bleed and bake resistance, poor chemical resistance, and fair lightfastness. They are used in all types of printing inks because of their clean, intense print tones and excellent physical ink properties and bleed resistance.

The manganese-precipitated product, ie, Manganese BON Red, exhibits significantly superior masstone lightfastness and is used in automotive and other high quality industrial enamels where durability is a prime consideration. It exhibits good bleed resistance but only fair bake resistance. The manganese BON Reds can be blended with molybdate orange to obtain a wide hue range of intense, durable reds.
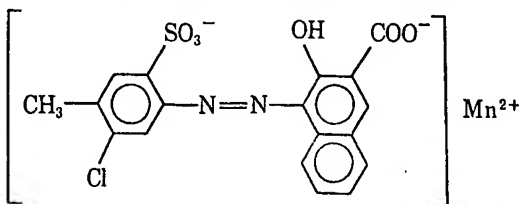
Manganese BON Red [12688-94-7]

Yellow BON Maroon.   Yellow BON Maroon (Pigment Red 55, CI 15820) is the manganese salt of the coupling from diazotized 4-chloroanthranilic acid with 3-hydroxy-2-naphthoic acid. It is a lightfast, yellow maroon with superior solvent bleed resistance and is suitable for automotive use or other outdoor finishes. It tends to change color on baking.
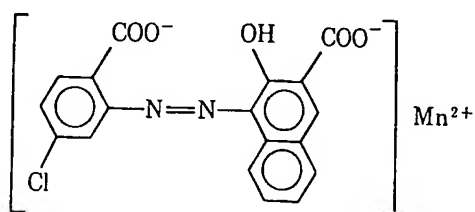

Yellow BON Maroon [5858-78-6]

Lithol Red 2G.   The manganese toner of Lithol Red 2G (Pigment Red 52) is intense in color and is used principally in blends with inorganic molybdate orange to produce durable red pigments. In such blends, it provides fair lightfastness but, generally, poor tint lightfastness. Solvent bleed resistance is good but chemical resistance is poor. The Lithol Red 2G manganese toner provides fair bake resistance even in molybdate-orange blends. As the calcium toner in printing inks, Lithol Red 2G exhibits tinctorial and other properties similar to those of Lithol Rubine.
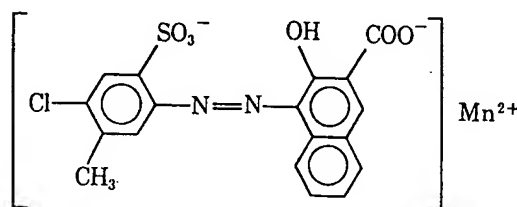
Pyrazolone Reds.   The pyrazolone reds are disazo pigments; they provide high color intensity, excellent masstone lightfastness, high transparency, and good bleed, bake, and chemical resistance (see Pyrazoles, pyrazolines, and pyrazolones). They are expensive and provide poor lightfastness in tint and metallic formulations. They are used in bicycle and motorcycle finishes.
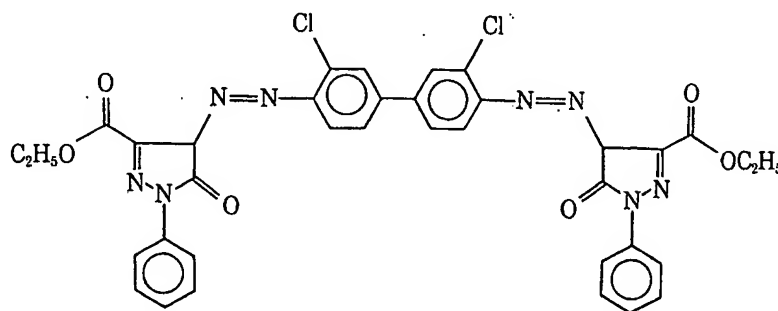
Pigment Red 38 [6358-87-8]

Naphthol Reds and Maroons. Naphthol Reds and Maroons are monoazo pigment dyes; they provide a wide range of colors from light reds to dark maroons, and are characterized by excellent alkali and general chemical resistance and good bake resistance.
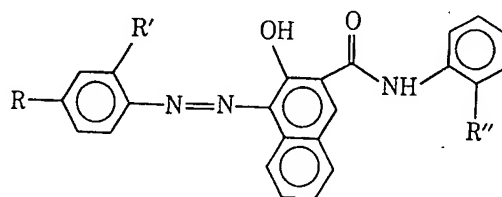
A maroon product which meets the durability requirements for automotive finishes is based on copper precipitation from the coupling of diazotized 4-nitroanthranilic acid with Naphthanil RL:
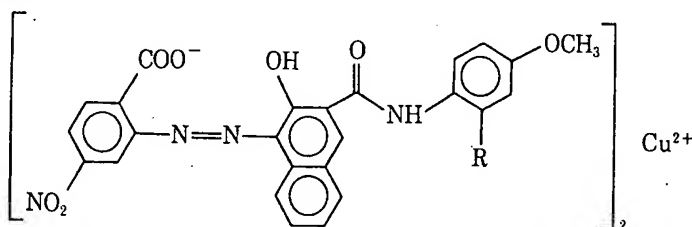
This maroon pigment is widely used in automotive metallic enamels because of its high transparency, excellent bleed and heat resistance, and excellent gloss retention when exposed to weather.

Azo Condensation Products. The search for pigments with improved properties, ie, lightfastness, heat stability, and bleed resistance, has resulted in commercial manufacture of a group of high molecular weight disazo products. Essentially, monoazo coupling products are prepared from diazotized aromatic amines and BON; these are condensed with aromatic diamines by the acid chlorides to produce high molecular weight products with improved working properties. Changing the original amines used for diazotization and the bridging diamines makes possible the manufacture of a broad range of colors (2–3). An example of the synthesis is illustrated below:
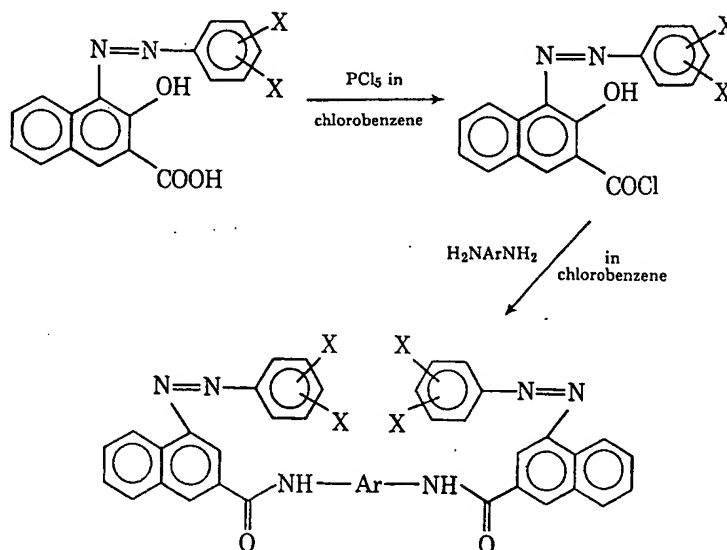
X = halogen, alkyl, alkoxy or carbethoxy groups

Azo Benzimidazolones.   The following are general structures for azo benzimidazolones.

X = ⬡— which may be substituted by halogen, nitro, alkyl or alkoxy groups
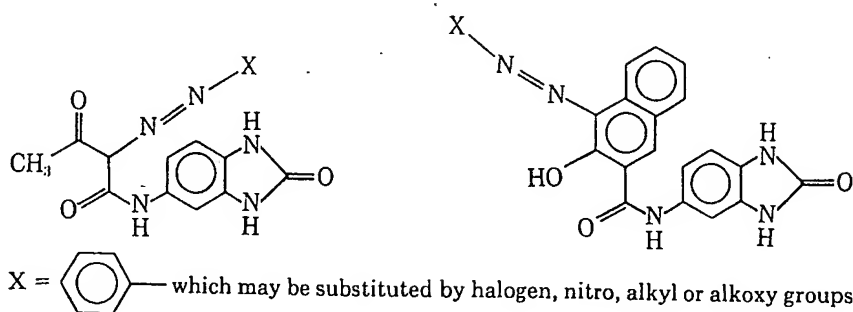
These pigments exhibit excellent solventfastness and are used extensively in paints and plastics.

Lakes.   Lakes are either a dry toner pigment that is extended or reduced with a solid diluent or an organic pigment that is prepared by the precipitation of a water-soluble dye on an adsorptive surface, which usually is an inorganic compound, eg, alumina hydrate. There is uncertainty in some instances as to whether the soluble dye precipitates on the surface of the inorganic compound to yield a dyed inorganic pigment, or whether it merely precipitates in the presence of the substrate, which serves no function in the insolubilization. A lake also forms from the precipitation of an insoluble salt from an acid or basic dye. Lakes from acid dyes usually precipitate upon addition of the soluble salts of the alkaline-earth metals, eg, barium or calcium, whereas the basic dyes form lakes by precipitation with the soluble salts of organic acids, eg, tannic acid, or with an inorganic acid, eg, phosphotungstic acid. Mordant dyes, eg, alizarin [72-48-0], form lakes by precipitation with the soluble salts of metals, eg, aluminum. Lakes have decreased in importance. The significant product for the printing-ink trade is Peacock Blue, the structure of which is given in Table 4.
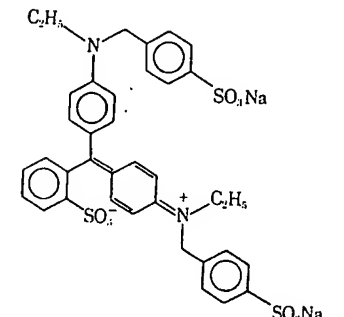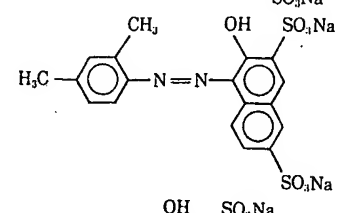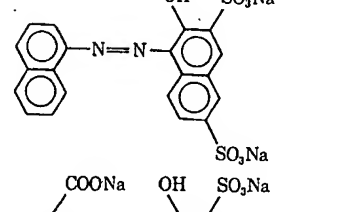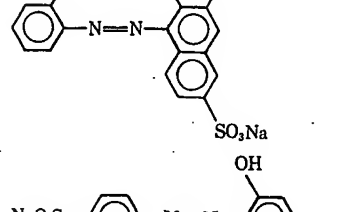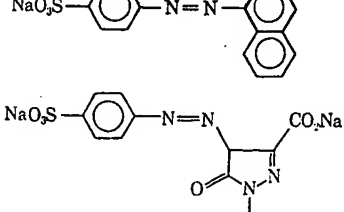
Alizarines.   Alizarine Red B or madder lake (Pigment Red 83) is a coordination complex of alizarin with alumina and calcium plus a sulfated castor oil and a phosphate (see Dyes, anthraquinone). It is an intense, deep bluish-red of fair lightfastness.
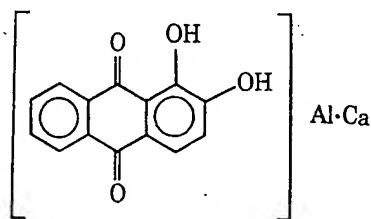

Alizarine Red B Lake [72-48-0]

Helio Fast Rubine 4BL.   Helio Fast Rubine 4BL (Pigment Violet 5) is a sulfonated quinizarin derivative and is used to shade pigments for organic coatings. It is an intense transparent color with good bleed and chemical resistance but poor tint lightfastness and bake resistance at high temperatures. The lake is formed from the reaction of the dye with alumina hydrate, which probably results in chelate formation.

Table 4. Typical Acid-Dye Pigment Lakes

Dye	CAS Registry Number	Chemical class	Structure
Peacock Blue	[14940-82-0]	triarylmethane	
Scarlet 2R	[3761-53-3]	azo	
Azo Bordeaux	[5858-33-3]	azo	
Pigment Scarlet 3B	[1836-22-2]	azo	
Orange 2	[633-96-5]	azo	
Tartrazine	[1934-21-0]	azo	

855
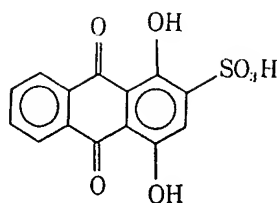
Helio Fast Rubine 4BL [145-48-2]

Basic-Dye Pigments. Basic dyes are characterized chemically by the presence of free or substituted amino groups in the dye molecule. A basic-dye pigment is the precipitated product of the reaction between a basic dye and either complex inorganic heteropoly acids to yield permanent basic-dye pigment or precipitants, eg, tannic acid, tartar emetic, clay, and fatty acid or rosin soaps to yield the nonpermanent or fugitive type.

Basic dyes generally are characterized by intense shade, high tinctorial strength, and low lightfastness. The latter is improved by precipitation with complex heteropoly acids; the products are used primarily in printing inks. Acids, eg, phosphotungstic (PTA), phosphomolybdic (PMA), and phosphotungstomolybdic (PTMA), are used as precipitants and make possible the retention of much of the inherent intensity and strength of the basic dye and impart insolubility and good lightfastness. Generally, of the three acid-derived pigment types, the PTA pigments are superior in lightfastness to the PMAs; although the latter exhibit greater strength. Despite their high costs and poor lightfastness, the basic-dye pigments continue to be used widely for their high strength and intensity. Representative basic dyes used in the pigment industry are listed in Table 5.

Phthalocyanines. Phthalocyanine pigments are characterized by excellent lightfastness, intensity, bleed and chemical resistance, extreme stability to heat, and exceptionally high tinting strength and are restricted to the blue and green regions of the spectrum. Other characteristics are excellent color value and working properties, low cost, and durability.

Copper Phthalocyanine Blue. Copper Phthalocyanine Blue (Phthalocyanine Blue, Pigment Blue 15) exists in at least two crystalline modifications; a red-shade blue alpha form, and the more stable green-shade beta form (see Phthalocyanine compounds). The redder alpha form must be stabilized during manufacture to prevent crystal growth or conversion to the green beta modification when in the presence of heat or aromatic solvents. Stabilization to crystal growth and to flocculation are effected by
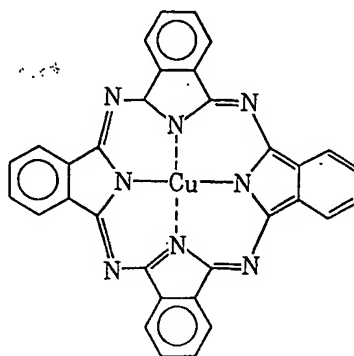
Copper Phthalocyanine Blue [147-14-8]

Table 5.   Typical Basic Dyes Used in Pigments

Dye	CAS Registry Number	Chemical class	Structure
Auramine O	[2465-27-2]	ketonimine	
Thioflavine T	[2390-54-7]	thiazine	
Rhodamine 6G	[57449-56-6]	xanthene[a]	
Malachite Green	[569-64-2]	triarylmethane[b]	

[a] A similar xanthene dye, which is used as a pigment, is Rhodamine B.

[b] Similar triarylmethane dyes, which are used as pigments, are Brilliant Green, Rhoduline Blue 6G (Setoglaucine), Methyl Violet B, Victoria Blue B, Victoria Pure Blue BO, and Crystal Violet [548-62-9].

special pigment-surface treatments or by the introduction of small amounts of chlorine into the pigment molecule.

Copper Polychlorophthalocyanine Green.   Copper Polychlorophthalocyanine Green (Phthalocyanine Green, Pigment Green 7) is derived from Pigment Blue 15 by means of chlorination, whereby 14–16 chlorine atoms are introduced into the molecule. The green provides the same excellent pigmentary qualities as the blue pigment. Although the former is resistant to crystal growth, special treatments are applied to overcome its tendency to flocculate in some paint systems.

Copper Polybromochlorophthalocyanines.   Copper polybromochlorophthalocyanines (Pigment Green 36) provide yellower shades of green than Copper Polychlorophthalocyanine. The degree of bromination is from 4–12 bromine atoms; the shade becomes more yellow with increasing bromine content. The performance characteristics of the products are similar to those of the polychloro green except that the polybromochloro provides lower tinting strength.

Quinacridones.   Quinacridone pigments offer generally outstanding fastness properties in the orange, maroon, scarlet, red, magenta, and violet color ranges. Because of their excellent pigmentary properties, they supplement Phthalocyanine Blues and Greens in extending the commercial availability of high grade pigments for applications that require excellent lightfastness. Representative commercial quinacridone pigments are listed in Table 6. Quinacridone may differ either in crystalline form or in particle size. The red, alpha crystalline form has not been commercialized and is the least stable thermodynamically of the three polymorphic forms.

Several syntheses for the commercial manufacture of quinacridone pigments are given in the patent literature (4). A typical synthesis is shown in Figure 1. Substituted quinacridones are prepared by using the appropriately substituted anilines.
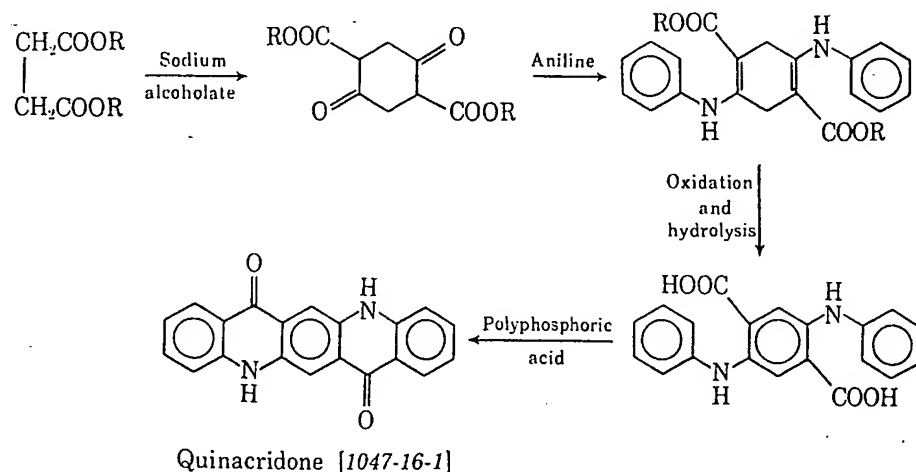

Quinacridone [1047-16-1]

Figure 1. Quinacridone synthesis.

The outstanding stability and insolubility of the quinacridone pigments are attributed to the high degree of intermolecular hydrogen bonding between the carbonyl ($-C=O$) and imino ($=NH$) groups in the crystal lattice. Several of the substituted quinacridone pigments also provide the desirable pigmentary characteristics of the unsubstituted quinacridones (see Table 6).

Quinacridone pigments are used in automotive finishes, for which their excellent

Table 6. Representative Commercial Quinacridone Pigments

Dye	CAS Registry Number	Color	Structure
quinacridone (QA)	[1047-16-1]	violet (beta form) red, blue shade (gamma form, small particle size) red, yellow shade (gamma form, large particle size)	
2,9-dimethylquinacridone	[980-26-7]	magenta	
quinacridonequinone	[1503-48-6]	maroon, yellow shade (solid solution)	QA +
4,11-dichloroquinacridone	[3089-16-5]	scarlet (solid solution)	QA +

durability including gloss retention justifies their high cost. Violet quinacridone is used extensively for toning white pigments and in blends with inorganic molybdate orange to formulate high quality, intense, durable, and low cost reds (5–6).

Dioxazines. Carbazole Dioxazine Violet (Pigment Violet 23) is a blue violet derived from amino-*N*-ethyl carbazole, and it exhibits exceptional strength and intensity and excellent heat and bleed resistance; however, it does show some solvent bleeding.
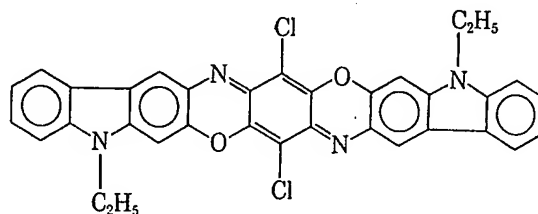
Carbazole Dioxazine Violet

Its lightfastness is excellent, even in light tints. Carbazole Dioxazine Violet is particularly suitable for shading phthalocyanine blues to redder shades and for toning whites to achieve a high degree of permanence.

Tetrachloroisoindolinones. Tetrachloroisoindolinones are marketed as Irgazins. The latter provide improved fastness properties over the original tetrachloroisoindolinones. Irgazins can be prepared from tetrachlorophthalimide by the following synthesis:

p-phenylenediamine
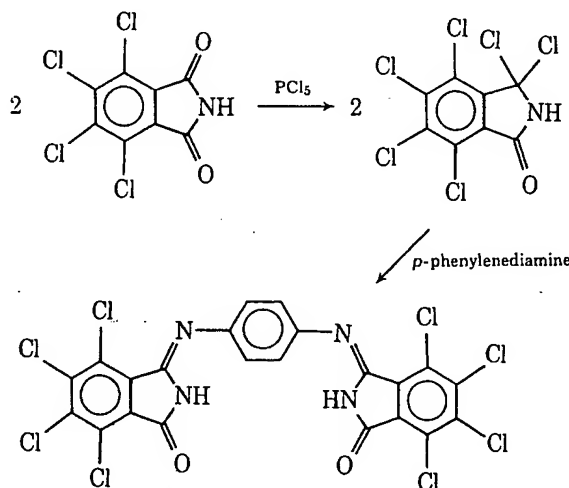
[55647-99-9]

A broad range of colors can be made by changing the diamine.

Vat-Dye Pigments. Vat dyes generally comprise a group of insoluble dyes that can undergo reduction to a water-soluble form and subsequent oxidation whereby the vat dye is regenerated without loss of color. In most cases, the colored organic compound contains two or more carbonyl ($>C=O$) groups, which are susceptible to reduction with sodium hydrosulfite in an alkaline medium yielding the leuco form

ONa
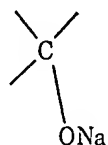
Generally, vat dyes must be modified chemically and physically so as to develop pigmentary strength and color intensity, which are required if they are to be used as pigments. The vat dyes cannot be defined in terms of color or properties, because they exist in a wide range of hues and exhibit fair-to-excellent pigmentary properties. Generally, they are expensive.
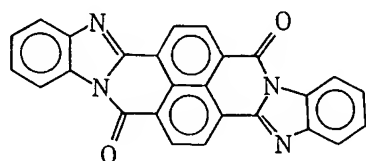
Thioindigos. The thioindigo vat-dye pigments provide a broad range of hues from a yellow shade of red to violet and, although tinctorially intense, they vary considerably in lightfastness, bleed resistance, and heat stability. The thioindigos that normally are used as pigments are symmetrical and contain chlorine or chlorine and methyl groups (see Table 7). The bordeaux, a dark maroon, is the most lightfast of the thioindigos, even in light tints, and exhibits excellent bleed resistance. Red Violet Y, also a maroon, provides good lightfastness and, in this respect, exceeds the pink, red, and magenta types. Red Violet RH provides moderate lightfastness and bleed resistance (7). The more lightfast thioindigo pigments are used in automotive finishes.

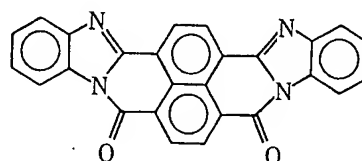**Table 7. Typical Thioindigo Pigments**

Dye	CAS Registry Number	Color	Structure
6,6'-dichloro-4,4'-dimethyl-thioindigo	[2379-74-0]	pink	
7,7'-dichlorothioindigo	[6371-11-5]	red	
4,4',7,7'-tetramethyl-5,5'-dichlorothioindigo	[2379-75-1]	magenta	
4,4'-dichloro-7,7'-dimethyl-thioindigo	[6371-31-9]	Red Violet Y	
4,4',7,7'-tetrachlorothioindigo	[14295-43-3]	bordeaux	
5,5'-dichloro-7,7'-dimethyl-thioindigo	[5462-29-3]	Red Violet RH	

Perinones. The perinone pigments are diimides of naphthalene-1,4,5,8-tetra-carboxylic acid. The diimide is formed by condensation of aromatic o-diamines with the acid or acid anhydride; the product usually is a mixture of the cis and trans isomers. The isomers are separated by taking advantage of the solubility characteristics of their respective salts.

Perinone Orange (Orange GR, Vat Orange 7, CI 71105) exhibits good bleed, good bake and chemical resistance, transparency, and moderate color intensity in metallic automotive paints. Although lightfastness is good in dark shades, it is poor in tint. Perinone Orange is used for shading automotive finishes. The use of Perinone Red is limited by its high solvent bleed.


Perinone Orange (trans isomer)
[4424-06-0]

Perinone Red (cis isomer)
[4216-02-8]

Perylenes. The perylene pigments are diimides of perylene-3,4,9,10-tetracar-boxylic acid and, although not as intense as the thioindigo pigments, generally are stronger and more resistant to chemicals, heat, and solvent bleeding. Perylene Scarlet (Vat Red 29, CI 71140 and Perylene Vermillion (Pigment Red 123) provide good tinting strength and moderate or high color intensity. Lightfastness in dark shades is good, although the vermillion shade provides moderate lightfastness in tint. Resistance to bleeding, baking, and chemicals is excellent. The scarlet and vermillion pigments are used in plastics.
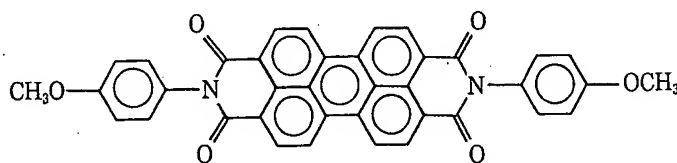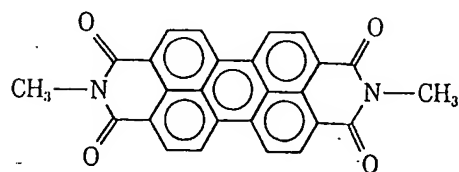

Perylene Scarlet [6424-77-7]
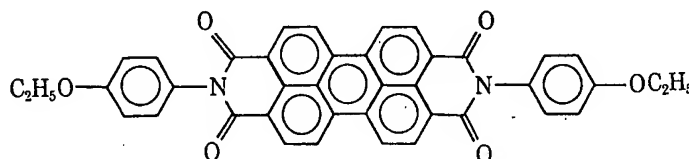
Perylene Vermillion [24108-89-2]

Perylenes Red, Maroon (Vat Red 23, CI 71130), and Bordeaux exhibit excellent lightfastness, in contrast with the Scarlet and Vermilion, and excellent resistance to baking and to reducing agents. The more lightfast perylenes are used in automotive finishes and in high grade industrial coatings.
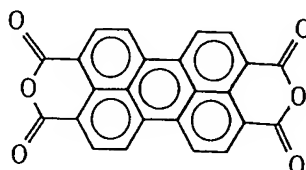
Perylene Maroon [5521-31-3]
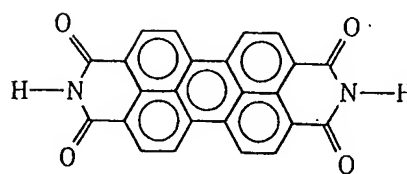
Perylene Bordeaux [81-33-4]

Perylene tetracarboxylic acid dianhydride is a useful red pigment.

Perylene dianhydride [128-69-8]

Anthraquinones. *Indanthrone Blue.* Indanthrone or Indathrene Blue (Vat Blue 6, CI 69825) is redder but less intense than the phthalocyanine blue pigments, and it provides good resistance to bleeding, baking, and chemicals (see Anthraquinone derivatives). It exhibits excellent durability, even in light tints, in all applications. In terms of durability, it is equivalent to Copper Phthalocyanine Blue, although it bronzes less in full shades in automotive paint systems. Although stronger than phthalocyanine blues, Indanthrone Blue is approximately two to three times more costly and is applied in automotive and other high quality finishes, in which redder blues are required or in which better bronzing in full shade is desired.
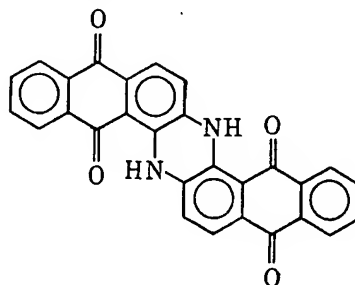
Indanthrone Blue [130-20-1]

Indanthrone exists in four polymorphic forms of which only one, the alpha modification, is used as a pigment. The other forms are not suitable, either in stability or tinctorial quality.

The partially chlorinated indanthrone blues also are used as pigments. Although greener than the unchlorinated ones, they do not exhibit equivalent bake resistance.
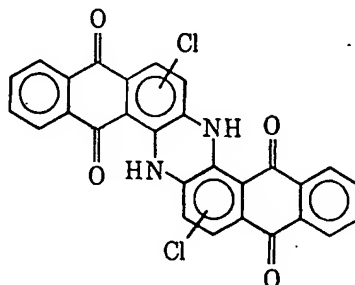
Isodibenzanthrone Violet. The lightfastness and durability characteristics of Isodibenzanthrone Violet (dichloroisodibenzanthrone, dichloroisoviolanthrone, Vat Violet 1, CI 60010) are comparable to those of the copper phthalocyanine pigments. Isodibenzanthrone is an intense blue violet with high tinting strength and excellent chemical resistance. It is somewhat sensitive to solvent bleeding. It is used to tone high quality blue and gray enamels and in the development of durable, intense automotive finishes.
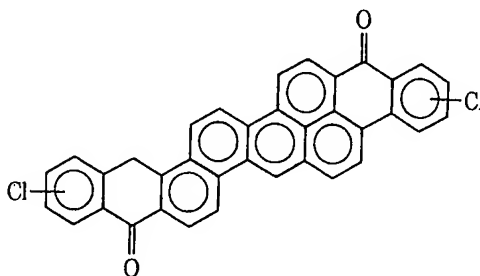
Isodibenzanthrone Violet [1324-55-6]

Dibromoanthranthrone Orange. Dibromoanthranthrone Orange (Orange RK, Vat Orange 3, CI 59300) offers excellent lightfastness at all tint levels and in metallic finishes. It exhibits good bake and chemical resistance but is sensitive to solvent bleeding. Its use is limited by its high cost and moderate color intensity.
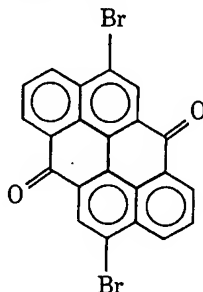
Dibromoanthanthrone Orange [4378-61-4]

Flavanthrone Yellow. Flavanthrone Yellow (Vat Yellow 1, CI 70600) is a red yellow of moderate intensity and provides good lightfastness in tint and metallic use and good resistance to bleeding, baking, and chemicals. It is high in cost and is inferior in bleed resistance to Anthrapyrimidine Yellow.
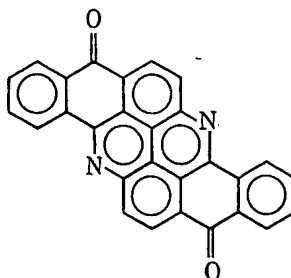
Flavanthrone Yellow [475-71-8]

Anthrapyrimidine Yellow. Anthrapyrimidine Yellow (Vat Yellow 20, CI 68420) is a transparent, green yellow with excellent lightfastness in tints and metallics and good resistance to bleeding, baking, and chemicals. It is high in cost and is characterized by low color intensity in automotive metallic finishes.
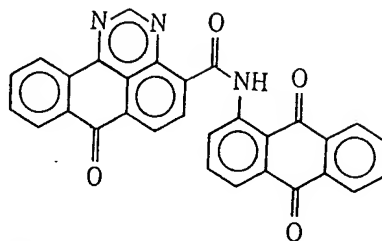
Anthrapyrimidine Yellow [4216-01-7]

Pigment Red 177.   Pigment Red 177 (CI 65300) is an amino anthraquinone pigment that provides excellent pigment properties, is expensive, and is used in plastics (8).

Pigment Red 177 [4051-63-2]

Miscellaneous.   Pigment Green B (Pigment Green 8), a complex iron salt of 1-nitroso-2-naphthol, is an inexpensive olive green, is stronger than the inorganic chrome greens, and exhibits high hiding and good alkali, bake, and bl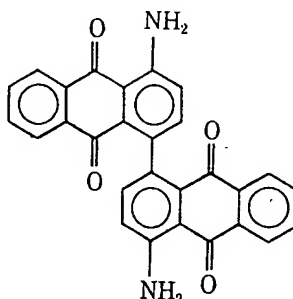eed resistance. Its color intensity is low and it exhibits poor tint lightfastness. It is used in emulsion paints, rubber, and paper coatings.
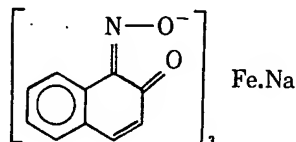
Pigment Green B [16413-80-9]

Alkali Blue (Pigment Blue 19) is the monosulfonic acid derivative of phenylated rosaniline (see Triphenylmethane and related dyes). Because of its high tinctorial strength, working properties, and low cost, it is used principally for the toning of carbon black that is intended for use in printing inks. Alkali Blue is moderately fast to light.
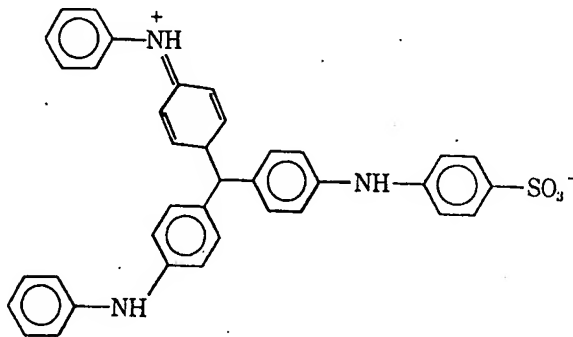
Alkali Blue [58569-23-6]

Production and Economic Aspects

U.S. production and sales during 1969–1979 are tabulated in Table 8; 1974–1978 imports and exports information is given in Table 9, and data regarding 1974–1978 exports by markets and 1974–1978 imports by principal sources are listed in Tables 10 and 11, respectively. α-Pigment Blue 15 and Pigments Red 144, Red 57:1, Yellow 93, Yellow 73, and Green 36 accounted for 41% of organic pigments imported into the United States in 1978 (12).

The following organic-pigment manufacturers reported their 1978 production

Table 8.   Organic Pigments (Toners and Lakers): U.S. Production and Sales, 1969–1979[a,b]

Year	Production, metric tons	Quantity, t	Sales unit value[c], $/kg	Value, 10³ $
Toners				
1969	25,995	21,489	6.02	129,310
1970	23,835	19,846	6.02	119,353
1971	24,987	20,070	6.31	126,564
1972	28,521	22,909	6.37	145,941
1973	30,368	26,758	6.68	178,583
1974	30,601	25,545	8.73	222,805
1975	21,647	18,497	9.83	182,067
1976	29,946	23,958	10.71	256,707
1977	30,905[c]	25,418	10.38	263,671
1978	33,814	27,856	11.02	315,352
1979[a]	39,515	21,960	12.50	374,305
Lakes				
1969	1,679	1,551	2.47	3,839
1970	1,804	1,548	2.34	3,612
1971	1,470	1,272	2.71	3,449
1972	1,369	1,229	2.78	3,402
1973	1,109	1,122	3.20	3,583
1974	1,059	981	5.09	5,007
1975	875	723	5.42	3,293
1976	774	632	6.94	4,382
1977	714	634	6.44	4,076
1978	621	419	7.23	3,030
1979[a]	513	378	8.47	3,204
Total				
1969	27,674	23,040	5.78	133,149
1970	25,639	21,394	5.75	122,965
1971	26,457	21,342	6.08	130,013
1972	29,890	24,138	6.19	149,343
1973	31,477	27,880	6.53	182,166
1974	31,660	26,526	8.60	227,812
1975	22,522	19,220	9.68	185,990
1976	30,720	24,590	10.60	261,089
1977	31,619[d]	26,052	10.27	267,747
1978	34,435	28,275	10.98	321,882
1979[a]	40,028	22,338	12.43	377,509

[a] Ref. 9.
[b] Ref. 10.
[c] Calculated from rounded figures.
[d] Revised figures for 1977.

Table 9.   Organic Pigments: U.S. Production, Imports, Exports, and Apparent Consumption, 1974–1978[a]

Year	Production[b]	Imports	Exports[c]	Apparent consumption	Ratio of imports, %
Quantity, t					
1974	31,660	3,693	6,675	28,678	12.9
1975	22,522	2,413	5,498	19,437	12.4
1976	30,720	3,124	6,579	27,266	11.5
1977	31,619	3,468	6,689	28,398	12.2[d]
1978	34,798	3,598	9,060	29,336	12.3
Value, 10^3 $					
1974	272,212	27,305	33,147	266,370	10.3
1975	217,977	20,278	25,062	213,193	9.5
1976	325,767	32,346	36,497	321,616	10.1
1977	324,835[d]	36,437	40,255	321,017[d]	11.4[d]
1978	382,046	41,721	56,426	367,341	11.4

[a] Ref. 10.

[b] Value of production estimated, based on unit value of sales.

[c] The export data shown are the official U.S. Department of Commerce statistics. Export statistics for 1968 through 1973, published in the *Synthetic Organic Chemicals, United States Production and Sales, 1977,* p. 139 (11), were estimated percentages of the official U.S. Department of Commerce statistics.

[d] Revised figures for 1977.

and/or sales data to the U.S. International Trade Commission: American Cyanamid Co.; American Hoechst Corp.: Industrial Chemical Div.; Apollo Colors, Inc.; BASF Wyandotte Corp.; Borden Inc.: Printing Ink Div., Pigments Div.; Binney and Smith, Inc.; Chemetron Corp.: Pigments Div. (Div. of BASF Wyandotte Corp. in 1979); CIBA-GEIGY Corp.; C. Lever Co., Inc.; E. I. du Pont de Nemours & Co., Inc.; Flint Ink Corp.: Cal/Ink Div.; Galaxie Chemical Corp.; Harmon Colors Corp. (Div. of Bayer); Harshaw Chemical Co. (Div. of Gulf Oil Corp.); Hercules, Inc. (Div. of CIBA-GEIGY Corp. in 1979); H. Kohnstamm & Co., Inc.; Indol Chemical Co., Inc. (Div. of Magruder Color Co., Ltd. in 1980); Industrial Color, Inc.; Inmont Corp. (Div. of United Technologies in 1979); Keystone Color Works, Inc.; Magruder Color Co., Inc.; Martin-Marietta Corp.: Sodyeco Div.; Max Marx Color & Chemical Co. (Div. of Johnson, Matthey & Co., Ltd in 1980); Mobay Chemical Corp.: Verona Dyestuff Div.; Paul Uhlich & Co., Inc.; Pope Chemical Corp.; Ridgeway Color and Chemicals; Sandoz Inc.: Colors & Chemical Div.; Sherwin-Williams Co.; Sterling Drug, Inc.: Hilton Davis Chemical Co. Div.; Sterling Drug, Inc.: Thomasset Colors Div.; Sun Chemical Corp.: Pigments Div.; Synalloy Corp.: Blackman-Uhler Chemical Div.; United Merchants & Manufacturers, Inc.: Roma Chemical Div.; USM Corp.: Bostik Div.

In 1980, the five principal producers of organic pigments were American Hoechst Corp.; BASF Wyandotte Corp.; CIBA-GEIGY Corp.; E. I. du Pont de Nemours & Co., Inc.; and Sun Chemical Corp.

The cost of raw materials and energy for the organic-pigments industry is expected to continue to rise because of international pressure on oil prices and changes in U.S. Government price controls of oil and gas. However, producers are emphasizing economical pigment manufacture that is subject of minimal government regulation. Types of organic pigments and an indication of the demand for them are listed in Table 12.

Table 10.   Organic Pigments: U.S. Exports, by Principal Markets, 1974–1978[a]

Market	1974	1975	1976	1977	1978
Quantity, t					
Australia	306	263	321	187	188
Belgium	181	113	270	366	569
Canada	1,241	1,190	1,223	850	1,663
France	226	121	271	187	229
FRG	223	230	166	375	519
Italy	494	262	544	376	576
Japan	326	297	631	480	621
Mexico	115	57	99	161	379
Netherlands	440	482	594	669	558
UK	513	343	327	525	699
other	2,441	2,017	1,944	2,206	2,765
Total	*6,506*	*5,375*	*6,390*	*6,382*	*8,766*
Value, 10^3 $					
Australia	1,400	985	1,341	1,293	1,180
Belgium	1,236	933	1,904	2,570	3,846
Canada	6,037	5,007	6,839	5,199	9,620
France	1,425	1,044	1,646	2,037	1,932
FRG	1,190	889	1,208	2,251	3,670
Italy	2,431	1,430	2,877	1,840	3,641
Japan	4,215	2,637	4,952	4,015	5,479
Mexico	654	528	682	1,058	2,372
Netherlands	1,643	1,738	3,218	3,817	3,610
UK	3,253	1,878	2,071	3,284	4,892
Venezuela	988	817	1,352	2,176	1,912
other	8,675	7,176	8,407	10,715	14,272
Total	*33,147*	*25,062*	*36,497*	*40,255*	*56,426*

[a] Ref. 10.

Standardization

Pigments can be standardized only in terms of performance, color, durability, and working properties and, often, only for the specific application or vehicle system for which the pigment is intended. A given pigment type may be dispersible in one system but poorly so in another, and exhibit different durability and color from one system to another. Thus, a given pigment chemical type often is marketed in a variety of forms, each of which is designed for a specific vehicle system or condition of use.

Workable pigment-product standards, which characterize properties in terms of acceptable ranges or limits and permissible deviations, are established by the pigment manufacturer insofar as they can be achieved practically in large-scale manufacture and as they are acceptable to the pigment user. The physical differences corresponding to the desired tolerances are not always easy to define nor, as in the case of durability and working properties, are they always subject to quick or accurate measurement.

Table 11.   Organic Pigments: U.S. Imports, by Principal Sources, 1974–1978[a]

Source	1974	1975	1976	1977	1978
Quantity, t					
Canada	179	361	239	322	259
Denmark	14	4	20	112	186
FRG	1,463	911	1,092	1,235	1,405
Italy	102	57	136	238	250
Japan	198	239	371	335	432
Switzerland	1,311	564	1,055	968	790
UK	122	136	93	93	110
other	304	141	119	166	166
Total	3,693	2,413	3,125	3,469	3,598
Value, 10^3 $					
Canada	835	981	1,343	1,621	1,213
Denmark	93	34	123	679	1,312
FRG	12,553	8,281	13,488	16,246	20,645
Italy	741	404	800	1,452	1,632
Japan	1,500	1,422	2,330	2,604	3,964
Switzerland	9,179	6,303	12,618	11,409	10,446
UK	1,056	1,789	700	1,041	1,109
other	1,348	1,064	944	1,385	1,400
Total	27,305	20,278	32,346	36,437	41,721

[a] Ref. 10.

Table 12.   Estimated Production of Organic Pigments (1979–1981), t[a]

Pigments	1979	1980	1981
carbon blacks	28,000	25,000	27,000
phthalo blues	1,600	1,500	1,590
phthalo greens	900	840	860
reds	1,200	1,170	1,200
yellows	230	210	220
others	540	490	530
Total	32,470	29,210	31,400

[a] Ref. 13.

Health and Safety Factors

The suspected or known health hazards associated with the use of some of the inorganic pigments, eg, some lead, chromium, and cadmium compounds, might lead to broader use of their organic color counterparts.

The proposed maximum content of polychlorobiphenyls (PCBs), eg, in diarylide yellows and phthalocyanines, allowed in any vehicle system is 50 ppm (14). Results from U.S. and European toxicological studies are listed in Table 13.

Uses

Organic pigments are used for decorative and/or functional effects, eg, in paints the pigment provides color and contributes significantly to the exposure durability

Table 13. U.S. and European Toxicological Studies on Diarylide Pigments

Pigment	Test species	Administration	Conclusion	Ref.
Yellow 12	rats	stomach intubation for 104 weeks	no evidence of carcinogenicity	15
	rats and mice	78 weeks in diet and 18–28 weeks observation	no evidence of carcinogenicity	16
	rats and mice	104 weeks in diet	no evidence of carcinogenicity and no evidence of metabolic splitting to free dichlorobiphenyls	17
	salmonella: microsome reversion	standard Ames test with and without 5–9 homogenate activation	no evidence of mutagenicity	18
Yellow 12 plus free DCB	rats and mice	104 weeks in diet	no evidence of carcinogenicity	17
Yellow 13	rabbits	single-dose stomach intubation	no evidence of metabolic splitting to free dichlorobiphenyls	17
	rabbits, rats, and monkeys	single-dose stomach intubation	no evidence of metabolic splitting to free dichlorobiphenyls	19
Yellow 16	rats and mice	104 weeks in diet	no evidence of carcinogenicity	17
Yellow 83	rats and mice	104 weeks in diet	no evidence of carcinogenicity	17
Orange 13	salmonella: microsome reversion	standard Ames test with and without 5–9 homogenate activation	no evidence of mutagenicity	18

of the paint film. Other functional effects include hiding power and high visibility, such as is obtained with daylight fluorescent pigments. Fluorescent pigments essentially are rigid solutions of fluorescent dyes that have been ground to pigmentary particle size, and suitable synthetic resins. They are used in various printing processes, textiles, plastics, and safety markings for vehicles and aircraft (see Luminescent materials).

The more important and established uses for pigment products include the coloration of the following materials and compositions: surface-coating compositions for interior, exterior, trade, and automotive applications, including oleoresinous (oil) paints, water-emulsion paints, and lacquers; leather and artificial-leather finishes, distempers, and lime colors; printing inks for rotogravure, lithographic, and flexographic systems, including inks for metal plate, foil, wallpaper, food wrappers, and packaging materials; textile printing inks for clothing, awnings, book cloth, etc; paper coloration by coating or beater dyeing; coloration of rubber, carbon paper, shoe polish, roofing granules, concrete and cement, ceramics, soaps and detergents, asphalt, molding powders, synthetic resins, and wax compositions; color-coating fertilizers and seeds; and laundry bluing. Coloration of textile fibers, eg, nylon, viscose, and cellulose acetate, is by mass pigmentation (see Dyes, application and evaluation—application). Organic pigments also are formulated for the coloration of plastics, including poly(vinyl chloride) sheet and plastisol top coatings, polyethylene, polypropylene, polystyrene, acrylonitrile–butadiene–styrene, etc. Numerous pigments are incorporated in artists' materials, eg, oils, crayons, chalk, colored pencils, modeling clay, etc.

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MILTON FYTELSON
Sandoz Colors & Chemicals

DISPERSED

A dispersed pigment concentrate is an extremely fine distribution of color pigment in any medium, ie, carrier, and is suitable for supplying color to surface printing, coating, or complete mass coloring (see Paint; Coatings). Because dispersing a pigment in a carrier generally is difficult and expensive, requiring specialized equipment and techniques, it often is performed on the smallest practical amount of material, ie, at the highest practical pigment concentration. The material produced after dispersion is the dispersed pigment concentrate; occasionally it is referred to as a pigment dispersion. Dispersed pigment concentrates are diluted, reduced, or extended to produce the final colored product.

Dispersion

Pigment dispersion is the minute distribution of a pigment throughout a dissimilar substance, a carrier (1). The carrier usually is a liquid or a solid which is at least deformable during processing. The process involves size reduction of the pigment to primary pigment particle size, reasonably complete wetting of all exposed pigment surfaces, and stabilization of the resulting system.

Reduction to primary particle size is necessary in order to develop the optimum visual and economic properties of the pigment and the optimum performance properties in application. The intensity or color strength of pigments is largely dependent on the exposed surface area; hence, the desirability of full reduction to the primary particle size. In practice, the extent of the reduction is determined by the nature of the pigment, the dispersion system and processing equipment, the product use requirements, and economics.

The maximum aggregate size that adversely affects physical properties is a small fraction of the thickness of the film, coating, or thin mass-colored material. For example, a fraction of up to one quarter might be tolerated for architectural paints or plastic films but smaller fractions, such as one fortieth, are required in the case of automotive finishes or colored monofilaments. In most cases, the maximum size applies to only a few of the largest aggregates; most aggregates must be reduced to a considerably smaller size for complete color-strength development, surface gloss, and film integrity and durability.

The optimum particle size to which a pigment should be reduced is the primary pigment particle. In dispersed pigments, the term primary pigment particle refers to individual crystals and the association of pigment crystals formed in the manufacturing process, such that the forces required to shear the primary particle into individual crystals are of the same order of magnitude as the forces that would shatter